REPORTS OF THE FINNISH ENVIRONMENT INSTITUTE 35 | 2019

Interlaboratory Proficiency Test 04/2019

Metals in natural water and sediment

Mirja Leivuori, Riitta Koivikko, Timo Sara-Aho, Teemu Näykki, Keijo Tervonen, Sari Lanteri, Ritva Väisänen and Markku Ilmakunnas

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ABSTRACT

Interlaboratory Proficiency Test 04/2019

Proftest SYKE carried out the proficiency test (PT) for analysis of elements in ground and domestic waters as well as in sediment in April 2019. The measurands for the synthetic sample and domestic and ground water samples were: Al, As, Cd, Co, Cr, Cu, Fe, Hg, Mn, Ni, Pb, Se, Ti, U, V, and Zn. In addition to the aforementioned, also measurands N_{tot}, P_{tot}, $S_{tot,}$ TC, and dry weight (Drw) were analysed from the sediment sample. In total 20 participants joined in the PT.

In this proficiency test 91 % of the results valuated based on z score were satisfactory when deviation of 10–25 % from the assigned value was accepted. From the results evaluated with E_n scores, 90 % were satisfactory. Basically, either the metrologically traceable concentration, the calculated concentration, the robust mean or the median of the results reported by the participants was used as the assigned value for the measurands.

Warm thanks to all the participants of this proficiency test!

Keywords: water analysis, sediment, metals, Al, As, Cd, Co, Cr, Cu, dry weight, Fe, Hg, Mn, Ni, N_{tot}, Pb, P_{tot}, Se, S_{tot}, TC, Ti, U, V, Zn, environmental laboratories, proficiency test, interlaboratory comparisons

TIIVISTELMÄ

Laboratorioiden välinen pätevyyskoe 04/2019

Proftest SYKE järjesti pätevyyskokeen ympäristönäytteitä analysoiville laboratorioille huhtikuussa 2019. Pätevyyskokeessa määritettiin synteettisistä näytteistä sekä talous- ja pohjavesinäytteistä testisuureet Al, As, Cd, Co, Cr, Cu, Fe, Hg, Mn, Ni, Pb, Se, Ti, U, V ja Zn. Sedimenttinäytteestä määritettiin näiden lisäksi myös N_{tot}, P_{tot}, $S_{tot,}$ TC sekä kuivapaino (Drw). Pätevyyskokeeseen osallistui yhteensä 20 osallistujaa.

Koko tulosaineistossa hyväksyttäviä z-arvolla arvioituja tuloksia oli 91 %, kun vertailuarvosta sallittiin 10–25 %:n poikkeama. Tuloksista, jotka arvioitiin E_n-arvolla, hyväksyttyjä oli 90 %. Testisuureen vertailuarvona käytettiin metrologisesti jäljitettävää pitoisuutta, laskennallista pitoisuutta, osallistujien ilmoittamien tulosten robustia keskiarvoa tai mediaania.

Kiitos pätevyyskokeen osallistujille!

Avainsanat: vesianalyysi, sedimentti, metallit, Al, As, Cd, Co, Cr, Cu, Fe, Hg, kuivapaino, Mn, Ni, N_{tot}, Pb, P_{tot}, Se, S_{tot}, TC, Ti, U, V, Zn, ympäristölaboratoriot, pätevyyskoe, laboratorioiden välinen vertailumittaus

SAMMANDRAG

Provningsjämförelse 04/2019

Proftest SYKE genomförde en provningsjämförelse i april 2019, som omfattade bestämningen av Al, As, Cd, Co, Cr, Cu, Fe, Hg, Mn, Ni, Pb, Se, Ti, U, V och Zn i syntetik sample, hushålls- och grundvatten och sedimentet, också N_{tot}, P_{tot}, $S_{tot,}$ TC och torrvikt (Drw) var bestämde i sedimentet. Tillsammans 20 laboratorier deltog i jämförelsen.

I jämförelsen 91 % av resultaten som värderas med hjälp z värdet var acceptabla, när total deviation på 10–25 % från referensvärdet tillåten. Resultaten som värderades med hjälp E_n värdet var 90 % acceptabla. Som referensvärde av analytens koncentration användes mest det metrologiska spårbara värdet, teoretiska värdet, robust medelvärdet, eller median av deltagarnas resultat.

Ett varmt tack till alla deltagarna i testet!

Nyckelord: vattenanalyser, sediment, metaller, Al, As, Cd, Co, Cr, Cu, Fe, Hg, Mn, Ni, N_{tot}, Pb, P_{tot}, Se, S_{tot}, TC, Ti, torrvikt, U, V, Zn, miljölaboratorier, provningsjämförelse

CONTENTS

1 Introduction

Proftest SYKE carried out the proficiency test (PT) for analysis of elements in ground and domestic waters and sediment in April 2019 (MET 04/2019). The measurands for the synthetic sample and domestic and ground water samples were: Al, As, Cd, Co, Cr, Cu, Fe, Hg, Mn, Ni, Pb, Se, Ti, U, V, and Zn. In addition to the aforementioned, also measurands N_{tot}, P_{tot}, $S_{tot,}$ TC, and dry weight (Drw) were analysed from the sediment sample. In total 20 participants joined in the PT. In the PT the results of Finnish participants providing environmental data for Finnish environmental authorities were evaluated. Additionally, other water and environmental laboratories were welcomed in the proficiency test.

Finnish Environment Institute (SYKE) is appointed National Reference Laboratory in the environmental sector in Finland. The duties of the reference laboratory include providing interlaboratory proficiency tests and other comparisons for analytical laboratories and other producers of environmental information. This proficiency test has been carried out under the scope of the SYKE reference laboratory and it provides an external quality evaluation between laboratory results, and mutual comparability of analytical reliability. The proficiency test has been carried out in accordance with the international standard ISO/IEC 17043 [1] and applying ISO 13528 [2] and IUPAC Technical report [3]. Proftest SYKE is accredited by the Finnish Accreditation Service as a proficiency testing provider (PT01, ISO/IEC 17043, www.finas.fi/sites/en). The organizing of this proficiency test is included in the accreditation scope of the Proftest SYKE.

2 Organizing the proficiency test

2.1 Responsibilities

Organizer

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The responsibilities in organizing the proficiency test

Mirja Leivuori	coordinator
Riitta Koivikko	substitute for coordinator
Keijo Tervonen	technical assistance
Markku Ilmakunnas	technical assistance
Sari Lanteri	technical assistance
Ritva Väisänen	technical assistance
Teemu Näykki	analytical expert (Hg, ID-ICP-MS)
Timo Sara-Aho	analytical expert (other measurands, ID-ICP-MS)

2.2 Participants

In total 20 participants joined in this proficiency test, 15 from Finland and 5 from other EU countries (Appendix 1). Altogether 95 % of the participants used accredited analytical methods at least for a part of the measurands. For this proficiency test, the organizing laboratory has the code 5 (SYKE, Helsinki, T003, ISO/IEC 17025, www.finas.fi/sites/en) in the result tables.

2.3 Samples and delivery

Four types of samples were delivered to the participants: synthetic, domestic and ground water as well as sediment samples. The sample preparation is described in details in the Appendix 2.

The synthetic sample A1M was prepared from the NIST traceable commercial reference material produced by Inorganic Ventures. The synthetic sample A1Hg was prepared by diluting from the NIST traceable AccuTrace™ Reference Standard produced by AccuStandard, Inc. The sample D2M was domestic water collected from the Helsinki area and the sample G3M was ground water collected from the southern Finland. To these samples additions of single element standard solutions (Merck CertiPUR®) were done when needed (Appendix 2). The water samples were acidified with nitric acid with the exception of samples for mercury, which were acidified with the hydrochloric acid.

The tested sediment sample S4M (after analysis: SC4 – oxygen combustion (only Hg) / SN4 – digestion with HNO_3 / SO4 – digestion with HNO_3 + HCl) was lake sediment from the Northern Savonia, eastern Finland used in previous Proftest SYKE PT MET 04/2013 [4]. Sediment was manually rehomogenized and divided into sub-samples. The homogeneity of the sediment sample was retested.

When preparing the samples, the purity of the used sample vessels was controlled. The randomly chosen sample vessels were filled with deionized water and the purity of the sample vessels was controlled after three days by analyzing Cd, Cu, Hg, and Zn. According to the test results all used vessels fulfilled the purity requirements.

The samples were delivered on 8 April 2019 to the participants abroad and on 9 April 2019 to the national participants. The samples arrived to the participants mainly on 10 April 2019.

The samples were requested to be measured as follows:

- Hg samples latest on 18 April 2019
- Other samples latest on 25 April 2019

The results were requested to be reported latest on 25 April 2019. Participants delivered the results accordingly. The preliminary results were delivered to the participants via ProftestWEB and email on 8 May 2019.

2.4 Homogeneity and stability studies

The homogeneity of the water samples was tested by analyzing Cd, Cr, Hg, Pb, Se, and Zn. More detailed information of the homogeneity studies is shown in Appendix 3. According to the homogeneity test results, all samples were considered homogenous. The synthetic samples were prepared from traceable certified reference materials. However, homogeneity of these was checked by parallel measurements of two samples.

The sediment sample was the same as in the previous Proftest SYKE PT MET 04/2013 [4]. The homogeneity of the sediment sample was tested after rehomogenization by parallel measurements (Cd, Cu, Hg, Mn, and Zn) of three samples and they confirmed the homogeneity of the sample.

Based on the earlier similar proficiency tests the samples are known to be stable over the given time period for the test.

2.5 Feedback from the proficiency test

The feedback from the proficiency test is shown in Appendix 4. The comments from the participants mainly dealt with the sample delivery. The comments from the provider were focused on the lacking conversancy to the given information with the samples and the reported detection limits. All the feedback is valuable and is exploited when improving the activities.

2.6 Processing the data

2.6.1 Pretesting the data

The normality of the data was tested by the Kolmogorov-Smirnov test. The outliers were rejected according to the Grubbs or Hampel test before calculating the mean. The results, which differed from the data more than $5 \times s_{rob}$ or 50 % from the robust mean, were rejected before the statistical results handling. If the result was reported as below detection limit, it has not been included in the statistical calculations.

More information about the statistical handling of the data is available from the Guide for participant [5].

2.6.2 Assigned values

The calculated values (NIST traceable) were used as the assigned values for the synthetic sample (A1M), with the exception of Hg and Pb. For Hg and Pb in the samples AIM, A1Hg, D2M, D2Hg, G3M, and G3Hg the results based on metrologically traceable isotope dilution (ID) ICP-MS technique were used as assigned values. The assigned value based on the ID-ICP-MS method is the mean of the homogeneity results and the test result (9–12 results). The ID-ICP-MS method is accredited in the scope of calibration laboratory (K054; www.finas.fi/sites/en). For the other samples and measurands the robust mean value ($n_{all} \geq 12$)

or the median value of the participants' results (n_{all} < 12) was used as the assigned value. If only one participant result was reported, no assigned value was set (N_{tot}: SO4).

The robust mean or the median of the participant results is not metrologically traceable assigned value. As it was not possible to have metrologically traceable assigned value, the robust mean or the median of the results was the best available value to be used as the assigned value. The reliability of the assigned value was statistically tested [2, 3].

The expanded uncertainty (*k=2*) for the calculated assigned values was estimated using standard uncertainties associated with individual operations involved in the preparation of the sample. The main individual source of the uncertainty was the uncertainty of the concentration in the stock solution.

When the robust mean or the median of the participant results was used as the assigned value, the uncertainty was calculated using the robust standard deviation or the standard deviation, respectively [2, 5]. For the metrologically traceable mercury and lead results, the uncertainty is the expanded measurement uncertainty of the ID-ICP-MS method.

The uncertainty of the calculated assigned value and the metrologically traceable value for metals in the synthetic samples varied between 0.4 and 3 %. When using the robust mean or the median of the participant results as the assigned value, the uncertainties of the assigned values were between 0.3 and 24 % (Appendix 5).

The assigned values have not been changed after reporting the preliminary results.

2.6.3 Standard deviation for proficiency assessment and results' evaluation

The standard deviation for proficiency assessment was estimated on the basis of the measurand concentration, the results of homogeneity and stability tests, the uncertainty of the assigned value, and the long-term variation in the former proficiency tests. The standard deviation for proficiency assessment based on z score evaluation ($2\times s_{pt}$, at the 95 % confidence level) was set to 10–25 % depending on the measurement. If the number of the results was low (n_{all}: 2–4, Hg: SC4; Ti: SN4, SO4; Se: SO4) and there was variability between the results, no standard deviation for proficiency assessment was given. **The standard deviations for the proficiency assessment have not been changed after reporting the preliminary results.**

When the number of reported results was low (n_{stat} < 6) or the variation between the results was high and the uncertainty was set for the assigned value, the performance was estimated by means of E_n scores ('*Error, normalized*').These are used to evaluate the difference between the assigned value and participant's result within their claimed expanded uncertainty. E_n scores are calculated:

$$(E_n)_i = \frac{x_i - x_{pt}}{\sqrt{U_i^2 + U_{pt}^2}}, \text{ where}$$

x_i = participant's result, x_{pt} = assigned value, U_i = the expanded uncertainty of a participant's result and U_{pt} = the expanded uncertainty of the assigned value.

Scores of E_n $-1.0 < E_n < 1.0$ should be taken as an indicator of successful performance when the uncertainties are valid. Whereas scores $E_n \geq 1.0$ or $E_n \leq -1.0$ could indicate a need to review the uncertainty estimates, or to correct a measurement issue.

When using the robust mean or the median of the participant results the assigned value, the reliability was tested according to the criterion $u_{pt} / s_{pt} \leq 0.3$, where u_{pt} is the standard uncertainty of the assigned value (the expanded uncertainty of the assigned value (U_{pt}) divided by 2) and s_{pt} is the standard deviation for proficiency assessment [1, 3]. When testing the reliability of the assigned value the criterion was mainly fulfilled and the assigned values were considered reliable.

The reliability of the standard deviation and the corresponding z score was estimated by comparing the deviation for proficiency assessment (s_{pt}) with the robust standard deviation (s_{rob}) or standard deviation (s, $n_{stat} < 12$) of the reported results (the criteria) [3]. The criterion $s_{rob} / s_{pt} < 1.2$ was mainly fulfilled.

In the following cases, the criterion for the reliability of the assigned value was not met and, therefore, the evaluation of the performance is weakened in this proficiency test:

Sample	Measurement
SN4	P_{tot}
SO4	As, Ni, Pb, P_{tot}
D2M	Fe

3 Results and conclusions

3.1 Results

The terms used in the results tables are presented in Appendix 6. The results and the performance of each participant are presented in Appendix 7 and the summary of the results in Table 1. The summaries of the z and E_n scores are shown in Appendices 8 and 9. In Appendix 10 the z scores are shown in the ascending order. The reported results with their expanded uncertainties (*k*=2) grouped according to the methods are presented in Appendix 11.

The robust standard deviations of the results varied mainly from 0.6 % to 22 % and the standard deviations of the sediment sample varied from 3.3 % to 30 % (Table 1). The robust standard deviation of results was lower than 10 % for 90 % of the results and lower than 20 % for 98 % of the results (Table 1). Standard deviations higher than 20 % apply mainly to the ground water sample (G3Hg, Table 1). The robust standard deviations for water samples (4.1–17 %) were approximately on the same level than in the previous almost similar proficiency tests MET 04/2017 and MET 05/2018, where the robust standard deviations varied from 3 % to 21 % for the water samples [6, 7]. For the sediment sample the robust standard deviations or the standard deviations were in the same range as in the previous similar PT MET 04/2013 [4], where the robust standard deviations varied from 0.6 % to 27 %. The robust standard deviation was not calculated when the number of results within the statistical evaluation was low (< 7, Table 1).

Table 1. The summary of the results in the proficiency test MET 04/2019.

Measurand	Sample	Unit	Assigned value	Mean	Rob. mean	Median	s_{rob} / s	s_{rob} % / s %	2 x s_{pt} %	n_{all}	Acc z %
Al	A1M	µg/l	335	331	330	332	23	6.8	10	16	75
	D2M	µg/l	37.9	37.9	37.9	37.6	2.1	5.7	15	15	86
	G3M	µg/l	14.3	14.4	14.3	14.2	1.2	8.3	20	14	85
	SN4	g/kg	22.4	20.8	-	22.4	*4.1*	*20*	-	4	-
	SO4	g/kg	25.9	25.1	-	25.9	*3.3*	*13*	25	6	83
As	A1M	µg/l	1.25	1.22	1.23	1.21	0.08	6.8	15	13	91
	D2M	µg/l	0.098	0.098	0.098	0.098	0.007	7.4	20	12	90
	G3M	µg/l	0.18	0.18	0.18	0.18	0.02	8.7	20	11	78
	SN4	mg/kg	6.65	6.36	-	6.65	*0.66*	*10*	-	5	-
	SO4	mg/kg	6.89	6.82	-	6.89	*0.95*	*14*	25	6	100
Cd	A1M	µg/l	0.75	0.73	0.73	0.74	0.06	8.6	15	15	79
	D2M	µg/l	0.31	0.31	0.31	0.31	0.02	5.1	15	14	92
	G3M	µg/l	0.15	0.15	0.16	0.15	0.01	5.1	15	13	91
	SN4	mg/kg	0.73	0.77	-	0.73	*0.13*	*16*	-	5	-
	SO4	mg/kg	0.69	0.67	-	0.69	*0.11*	*16*	-	6	-
Co	A1M	µg/l	2.25	2.17	2.18	2.17	0.10	4.4	10	13	92
	D2M	µg/l	0.32	0.32	0.32	0.32	0.02	7.6	15	12	90
	G3M	µg/l	0.22	0.22	0.21	0.22	0.01	5.0	15	11	88
	SN4	mg/kg	34.0	34.0	-	34.0	*2.1*	*6.2*	-	5	-
	SO4	mg/kg	35.7	35.1	-	35.7	*2.6*	*7.3*	20	6	100
Cr	A1M	µg/l	4.50	4.40	4.38	4.40	0.21	4.8	15	15	93
	D2M	µg/l	1.57	1.56	1.56	1.57	0.06	4.0	15	12	91
	G3M	µg/l	0.54	0.55	0.54	0.54	0.03	5.0	15	12	100
	SN4	mg/kg	56.3	55.3	-	56.3	*4.9*	*8.9*	25	6	100
	SO4	mg/kg	58.9	58.9	-	58.9	*6.1*	*10*	25	6	100
Cu	A1M	µg/l	12.5	12.0	12.0	12.1	1.1	9.1	10	15	80
	D2M	µg/l	56.8	56.9	56.8	55.8	3.2	5.6	15	14	100
	G3M	µg/l	3.57	3.55	3.57	3.51	0.28	7.7	20	13	100
	SN4	mg/kg	68.1	66.4	-	68.1	*3.4*	*5.2*	20	6	100
	SO4	mg/kg	70.2	69.0	-	70.2	*3.2*	*4.6*	20	6	100
Drw	S4M	%	98.1	98.0	98.1	98.1	0.6	0.6	5	11	100
Fe	A1M	µg/l	175	176	175	173	8	4.8	10	17	88
	D2M	µg/l	37.5	37.7	37.5	37.1	3.1	8.3	15	16	87
	G3M	µg/l	17.5	17.6	17.5	17.4	1.6	9.1	20	14	92
	SN4	g/kg	32.9	33.1	-	32.9	*3.7*	*11*	20	6	83
	SO4	g/kg	34.5	34.6	-	34.5	*2.7*	*7.7*	20	6	100
Hg	A1Hg	µg/l	0.15	0.15	0.15	0.16	0.02	14.5	20	13	85
	D2Hg	µg/l	0.075	0.074	0.079	0.075	0.014	17.6	25	12	70
	G3Hg	µg/l	0.050	0.053	0.056	0.054	0.012	21.5	25	12	70
	SC4	mg/kg	0.67	0.67	-	0.67	*0.03*	*3.8*	-	2	-
	SN4	mg/kg	0.73	0.73	-	0.73	*0.03*	*4.1*	-	5	-
	SO4	mg/kg	0.70	0.71	-	0.70	*0.06*	*8.7*	20	7	86
Mn	A1M	µg/l	43.5	43.5	43.5	43.7	2.2	5.2	10	15	100
	D2M	µg/l	15.6	15.8	15.6	15.9	1.1	6.8	15	15	87
	G3M	µg/l	4.01	4.02	4.01	4.02	0.22	5.4	15	13	100
	SN4	mg/kg	630	639	-	630	*37*	*5.7*	15	6	100
	SO4	mg/kg	702	705	-	702	*31*	*4.3*	15	6	100

Table 1. The summary of the results in the proficiency test MET 04/2019.

Measurand	Sample	Unit	Assigned value	Mean	Rob. mean	Median	s_{rob} / *s*	s_{rob} % / *s* %	2 x s_{pt} %	n_{all}	Acc z %
Ni	A1M	µg/l	7.25	7.18	7.05	7.20	0.51	7.2	15	14	93
	D2M	µg/l	0.54	0.55	0.55	0.54	0.02	2.8	20	12	78
	G3M	µg/l	1.56	1.55	1.56	1.56	0.11	7.0	15	12	82
	SN4	mg/kg	48.6	47.3	-	48.6	*2.7*	*5.6*	-	5	-
	SO4	mg/kg	47.3	47.7	-	47.3	*4.1*	*8.6*	20	6	100
N_{tot}	SN4	g/kg	4.74	4.62	-	4.74	*0.26*	*5.6*	-	6	-
	SO4	g/kg	-	4.83	-	4.83	-	-	-	1	-
Pb	A1M	µg/l	4.24	4.19	4.22	4.20	0.16	3.8	15	15	92
	D2M	µg/l	2.18	2.13	2.13	2.18	0.13	6.0	15	14	100
	G3M	µg/l	0.57	0.56	0.56	0.56	0.03	5.8	15	13	91
	SN4	mg/kg	28.7	28.5	-	28.7	*1.9*	*6.7*	-	5	-
	SO4	mg/kg	25.8	26.0	-	25.8	*3.0*	*12*	25	6	100
P_{tot}	SN4	g/kg	1.09	1.10	1.10	1.09	0.13	11.4	20	7	100
	SO4	g/kg	1.11	1.12	-	1.11	*0.10*	*9.1*	20	6	100
Se	A1M	µg/l	1.25	1.22	1.23	1.21	0.11	9.3	15	12	82
	D2M	µg/l	0.52	0.53	0.53	0.52	0.03	5.7	15	11	100
	G3M	µg/l	1.90	1.92	1.88	1.90	0.10	5.3	15	11	90
	SN4	mg/kg	2.60	2.66	-	2.60	*0.80*	*30*	-	6	-
	SO4	mg/kg	2.81	3.04	-	2.81	*1.9*	*62*	-	6	-
S_{tot}	SN4	g/kg	4.37	4.25	-	4.37	*0.47*	*11*	-	4	-
	SO4	g/kg	4.00	4.08	-	3.99	*0.38*	*9.3*	-	5	-
TC	S4M	g/kg	87.7	87.3	-	87.7	*6.1*	*7.0*	-	5	-
Ti	A1M	µg/l	22.5	21.7	21.7	21.6	0.9	4.0	10	9	100
	D2M	µg/l	5.26	5.30	5.26	5.26	0.23	4.3	15	9	88
	G3M	µg/l	16.0	16.1	16.1	16.0	1.1	6.7	15	8	100
	SN4	mg/kg	1800	1681	-	1800	*244*	*11*	-	3	-
	SO4	mg/kg	1820	1758	-	1820	*460*	*26*	-	3	-
U	A1M	µg/l	0.65	0.63	0.64	0.65	0.03	5.0	15	12	92
	D2M	µg/l	0.11	0.11	0.11	0.11	0.01	11.3	25	12	91
	G3M	µg/l	2.29	2.28	2.28	2.29	0.16	6.8	15	11	100
	SN4	mg/kg	3.30	3.27	-	3.30	*0.32*	*9.8*	-	5	-
	SO4	mg/kg	3.61	3.39	-	3.61	*0.59*	*17*	-	3	-
V	A1M	µg/l	4.25	4.05	4.05	4.03	0.15	3.8	10	12	100
	D2M	µg/l	3.11	3.06	3.07	3.11	0.16	5.1	15	12	100
	G3M	µg/l	0.88	0.88	0.87	0.88	0.06	7.2	15	11	100
	SN4	mg/kg	58.4	55.0	-	58.4	*6.1*	*11*	-	5	-
	SO4	mg/kg	62.7	61.4	-	62.7	*6.5*	*11*	-	6	-
Zn	A1M	µg/l	33.5	33.0	33.1	33.0	1.4	4.1	10	15	80
	D2M	µg/l	10.2	10.2	10.2	10.2	0.5	4.4	15	13	92
	G3M	µg/l	5.40	5.35	5.40	5.22	0.37	6.8	15	12	92
	SN4	mg/kg	212	214	-	212	*7.1*	*3.3*	15	6	100
	SO4	mg/kg	203	208	-	203	*11*	*5.5*	-	5	-

Rob. mean: the robust mean, s_{rob}: the robust standard deviation, *s:* the standard deviation, s_{rob} %: the robust standard deviation as percent, *s%* : the standard deviation as percent, $2 \times s_p$ %: the total standard deviation for proficiency assessment at the 95 % confidence level, Acc z %: the results (%), where $|z| \leq 2$, n(all): the total number of the participants.

3.2 Analytical methods

The participants were allowed to use different analytical methods for the measurands in the PT. The used analytical methods and results of the participants grouped by methods are shown in more detail in Appendix 11. The statistical comparison of the analytical methods was possible for the data where the number of the results was ≥ 5. The statistically significant differences between the results are shown in Appendix 12.

Effect of sample pretreatment on elemental concentrations in sediment sample

The sediment sample S4M was measured using pretreatment and the results from different pretreatment procedures were processed separately in data handling. Almost equally the participants (from four to six participants depending on the measurand) measured the sediment sample after nitric acid digestion (SN4) and after acid mixture of HNO_3+HCl for the digestion (SO4 Table 1, Appendix 11). For Hg measurements five participants used the nitric acid digestion (SN4), six used acid mixture of HNO_3+HCl (MO4) for the digestion and two participants used the oxygen combustion pretreatment (MC4).

The difference between the average concentrations of elements measured after different sample preparation steps was tested using the t-test. Statistically significant difference was observed for Mn analyses where acid digestion with nitric acid (SN4) gave significantly lower results (639 ± 37 mg/kg, mean ± standard deviation) than acid digestion with acid mixture of HNO_3+HCl (SO4, 705 ± 31 mg/kg, Appendix 12).

Effect of measurement methods on elemental results

The most commonly used analytical methods were ICP-MS and ICP-OES. Only one participant used FAAS or GAAS techniques for some measurands (Appendix 11). The difference between the average concentrations of metals measured by different measurement methods was tested using the t-test. In the statistical treatment no significant differences were observed, when the number of results were high enough for the statistical comparison.

N_{tot} in the sediment sample (SN4, SO4) was mainly measured using N-Kjeldahl or similar method or by C, H, N-analyzer. TC in the sediment sample S4M was mainly measured by C, H, N-analyzer (Appendix 11).

As a general note, a low recovery may be an indication of loss of measurand which can occur during sample pretreatment (e.g. volatilization during acid digestion) or measurement (e.g. GAAS analysis). It may also be caused by incorrect background correction (ICP-OES) or matrix effects. Recoveries that are too high may be caused by spectral interferences (overlapping wavelengths in emission spectrometry, polyatomic or isobaric interferences in mass spectrometry), matrix effects or contamination. Matrix effects can often be overcome by matrix matching the calibration standards however; this is often difficult with environmental samples since the elemental concentrations vary a lot even within the same sample type.

According to the results of this PT, majority of the participant's results of Co, Ti, and V remained lower than the assigned values for the sample A1M. However, the differences were generally within the reported measurement uncertainties of the participants.

Effect of measurement methods on mercury results

For the analysis of mercury, ICP-MS was the most often used method of analysis. That was followed by CV-AFS and CV-AAS. Other used methods were CV-ICP-MS, ICP-OES, and direct combustion (Appendix 11). Based on visual estimation no differences between the used measuring methods were found. For the sediment sample, aqua regia digestion (SO4) was slightly more often used than nitric acid digestion (SN4).

Like other metal determinations, mercury results are also affected by digestion procedures used (acids and oxidation reagents, their concentration, volumes and purities, digestion temperature and time). For water samples hydrochloric acid is recommended for sample preservation and BrCl is recommended for oxidation of mercury species.

Generally, the differences in mercury results are most likely due to different pretreatment procedures, provided a measurement technique sensitive enough is used. Cold vapour techniques are recommended, especially for natural water matrices with low concentrations. CV-AFS and CV-ICP-MS have superior detection capability compared to CV-AAS or CV-ICP-OES.

3.3 Uncertainties of the results

At maximum 75 % of the participants reported the expanded uncertainties (k=2) with their results for at least some of their results (Table 2, Appendix 13). Several approaches were used for estimating the measurement uncertainty (Appendix 13). The most commonly used approach was based on the internal quality data with sample replicates and the method validation data [8]. MUkit measurement uncertainty software for the estimation of the uncertainties was used by at maximum five participants (Appendix 13) [9]. The free software is available in the webpage: www.syke.fi/envical/en. Generally, the used approach for estimating measurement uncertainty did not make definite impact on the uncertainty estimates

The range of the reported uncertainties varied between the measurements and the sample types. As can be seen in Table 2, some of the participants have over-estimated their expanded ($k=2$) measurement uncertainty. Very high measurement uncertainties (i.e. 50 % or higher) should not exist, unless the measured concentration is near to the limit of quantification. The reported expanded uncertainties below 5 % commonly could be considered unrealistic uncertainty value for routine laboratories.

In order to promote the enhancement of environmental measurements' quality standards and traceability, the national quality recommendations for data entered into the water quality registers have been published in Finland [10]. The recommendation for measurement uncertainties in natural waters is 15 % for the measurands of this proficiency test. In this proficiency test some of the participants had their measurement uncertainties within this limit, while some did not achieve it. However, harmonization of the uncertainties estimation should be continued.

Table 2. The range of the expanded measurement uncertainties (k=2, U_i%) reported by the participants.

Measurand	A1M/A1Hg, %	D2M/D2Hg, %	G3M/G3Hg, %	SC4/S4M/SN4/SO4, %
Al	6-30	10-30	10-30	10-30
As	10-36	19-75	10-42.6	15-50
Cd	10-38	10-68	10-23	10-50
Co	9-20	10-40	10-23	15-40
Cr	10-72	10-27	10-25	15-26
Cu	9-20	9-20	10-30	15-50
Drw	-	-	-	1-30
Fe	8-33	8-33	8-35	10-30
Hg	15-30	15-30	15-30	15-50
Mn	7-20	7-20	8-25	10-25
Ni	10-25	10-25	10-39	15-35
N_{tot}	-	-	-	7-20
Pb	10-38	10-25	10-25	15-35
P_{tot}	10-38	10-25	10-25	15-35
Se	15-30	15-40	15-30	20-50
S_{tot}	-	-	-	10-30
TC	-	-	-	2-30
Ti	10-20	10-42	10-20	15-59
V	8-21	8-38	8-21	17-30
Zn	8-29	8-31	10-29	12-25

4 Evaluation of the results

The performance evaluation of the participants was based on the z scores, which were calculated using the assigned values and the standard deviation for the performance assessment (Appendix 6). Additionally, some of the results were evaluated using E_n scores. The z and E_n scores were interpreted as follows:

Criteria	Performance
$\lvert z \rvert \leq 2$	Satisfactory
$2 < \lvert z \rvert < 3$	Questionable
$\lvert z \rvert \geq 3$	Unsatisfactory
$-1.0 < E_n < 1.0$	Satisfactory
$E_n \leq -1.0$ or $E_n \geq 1.0$	Unsatisfactory

In total, 91 % of the z score results were satisfactory, when deviation 10–25 % from the assigned value was accepted (Appendix 8). In total, 90 % of the E_n score results were satisfactory for the sediment sample (Appendix 9).

Altogether 95 % of the participants used accredited analytical methods at least for a part of the measurands and 93 % of their results were satisfactory. The summary of the performance evaluation and comparison to the previous performance is presented in Table 3.

The satisfactory results based on z scores varied between 89 and 97 % for the tested sample types (Table 3). The share of satisfactory results in the synthetic sample A1M was the lowest for Al, about 75 %. Totally the share was in the same level as in the previous similar proficiency test in 2018 (Table 3) [7].

For the domestic water samples (D2M, D2Hg) all results for Cu, Pb, Se and V were satisfactory, while for Hg the share of the satisfactory results was 70 %. For the ground water samples (G3M, G3Hg) all results for Cr, Cu, Mn, Ti, U and V were satisfactory, and for Hg the recovery was the lowest 70 %. In this proficiency test the share of satisfactory results was almost in the same level as in the previous proficiency tests (Table 3) [6, 7].

For the sediment sample digested with nitric acid (SN4) the number of results was low, and thus the performance was evaluated based on the z or E_n scores (Table 1, Appendix 9). In total, 89–97 % of the evaluated results were satisfactory (Table 3). The performance of the sediment results obtained after aqua regia digestion (HNO_3+HCl, SO4), was also evaluated based on z or E_n scores depending the number of results (Table 1, Appendix 9). In this case 92–97 % of the results were satisfactory (Table 3). The overall performance was slightly higher than in the previous PT MET 04/2013, where the same sediment sample was used [4]. However, in this PT there were less than half of participant results in the previous PT in 2013.

Table 3. Summary of the performance evaluation in the proficiency test MET 04/2019.

Sample	Satisfactory results (%)	Accepted deviation from the assigned value (%)	Remarks
A1M, A1Hg	89	10–20	• Difficulties in measurements for Al and Cd, < 80% satisfactory results. • In the previous PT MET 05/2018 the performance was satisfactory for 90 % of the results [7].
D2M, D2Hg	90	15-25	• Mainly good performance. • Only approximate assessment for Fe. • Difficulties in measurements for Hg and Ni, < 80% satisfactory results. • In the previous PT MET 04/2017 the performance was satisfactory for 92 % of the results, when accepting the deviation of 10-25 % from the assigned value [6].
G3M, G3Hg	91	15-25	• Mainly good performance. • Difficulties in measurements for As, < 80% satisfactory results. • In the previous PT MET 05/2018 the performance was satisfactory for 86 % of the results, when accepting the deviation of 10-25 % from the assigned value respectively [7].
SN4 SC4	Based on z score: 97 Based on E_n score: 89	15-25	• Mainly good performance. • Only approximate assessment for P_{tot}. • In the previous PT MET 04/2013 the performance was satisfactory based on z scores for 81 % of the results when accepting the deviation of 20-35 % from the assigned value [4].
SO4	Based on z score: 97 Based on E_n score: 92	15-25	• Mainly good performance. • Only approximate assessment for As, Ni, Pb, P_{tot}. • In the previous PT MET 04/2013 the performance was satisfactory based on z scores for 91 % of the results when accepting the deviation of 15-30 % from the assigned value [4].

For the sediment sample digested with nitric acid, SN4, all results for Cr, Cu, Mn, P_{tot}, and Zn were satisfactory based on z score. Similarly for aqua regia digested sediment sample SO4 all results for As, Co, Cr, Cu, Fe, Mn, Ni, Pb and P_{tot} were satisfactory.

5 Summary

Proftest SYKE carried out the proficiency test (PT) for analysis of elements in ground and domestic waters and sediment in April 2019 (MET 04/19). The measurands for the synthetic sample and domestic and ground water samples were: Al, As, Cd, Co, Cr, Cu, Fe, Hg, Mn, Ni, Pb, Se, Ti, U, V, and Zn. In addition to the aforementioned, also measurands N_{tot}, P_{tot}, $S_{tot,}$ TC, and dry weight (Drw) were analysed from the sediment sample. In total 20 participants joined in the PT.

The calculated values (NIST traceable) were used as the assigned values for the synthetic samples (A1M) with the exception of Hg and Pb. For Hg and Pb in the samples AIM, A1Hg, D2M, D2Hg, G3M, and G3Hg the results based on metrologically traceable isotope dilution (ID) ICP-MS technique were used as assigned values. For the other samples and measurands the robust mean value ($n_{all} \geq 12$) or the median value of the participants' results ($n_{all} < 12$) was used as the assigned value.

The uncertainties of the calculated assigned values and the metrologically traceable values for metals in the synthetic samples varied between 0.4 and 3 %. When using the robust mean or the median of the participant results as the assigned value, the uncertainties of the assigned values were between 0.3 and 24 %

The evaluation of the performance was based on the z and E_n scores. In this PT, 91 % of the z score results were satisfactory, when deviation 10–25 % from the assigned value was accepted. In total, 90 % of the E_n score results were satisfactory for the sediment sample. About 95 % of the participants used accredited methods and 93 % of their results were satisfactory.

6 Summary in Finnish

Proftest SYKE järjesti ympäristönäytteitä analysoiville laboratorioille pätevyyskokeen huhtikuussa 2019. Pätevyyskokeessa määritettiin synteettisistä näytteistä sekä talous- ja pohjavesinäytteistä testisuureet Al, As, Cd, Co, Cr, Cu, Fe, Hg, Mn, Ni, Pb, Se, Ti, U, V ja Zn. Sedimenttinäytteestä määritettiin näiden lisäksi myös N_{tot}, P_{tot}, $S_{tot,}$ TC sekä kuivapaino (Drw). Pätevyyskokeessa oli yhteensä 20 osallistujaa.

Testisuureen vertailuarvona käytettiin laskennallista pitoisuutta, osallistujien tulosten robustia keskiarvoa tai mediaania. Lyijylle ja elohopealle käytettiin metrologisesti jäljitettävää tavoitearvoa osalla testinäytteistä. Vertailuarvolle laskettiin laajennettu epävarmuus 95 % luottamusvälillä. Vertailuarvon laajennettu epävarmuus oli välillä 0,4–3 % laskennallista tai metrologisesti jäljitettävää pitoisuutta vertailuarvona käytettäessä ja muilla välillä 0,3–24 %.

Pätevyyden arviointi tehtiin z- ja E_n-arvojen avulla. Koko aineistossa hyväksyttäviä tuloksia z-arvoilla arvioituna oli 91 %, kun tulosten annettiin vaihdella 10–25 % vertailuarvosta. E_n-arvoilla arvioiduista sedimenttinäytteen tuloksista 90 % oli hyväksyttyjä. Noin 95 % osallistujista käytti akkreditoituja määritysmenetelmiä ja näistä tuloksista oli hyväksyttäviä 93 %.

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APPENDIX 1: Participants in the proficiency test

Country	Participant
Finland	Eurofins Ahma Oy Seinäjoki
	Eurofins Ahma Oy, Oulu
	Eurofins Environment Testing Finland Oy, Lahti
	Fortum Waste Solutions Oy, Riihimäki
	KVVY Tutkimus Oy, Tampere
	Kymen Ympäristölaboratorio Oy
	Lounais-Suomen vesi- ja ympäristötutkimus Oy, Turku
	Luonnonvarakeskus, Viikki B2-laboratorio
	MetropoliLab Oy
	Savo-Karjalan Ympäristötutkimus Oy, Kuopio
	SeiLab Oy Seinäjoen toimipiste
	SGS Finland Oy, Kotka
	STUK, Ympäristön säteilyvalvonta, Valvonta ja Mittaus (VAM)
	SYKE, Helsingin toimipaikka
	SYNLAB Analytics & Services Finland Oy
France	PearL, Limoges Cedex, France
Sweden	Erkenlaboratoriet
	INOVYN Sverige Ab
	Stockholm University, ACES
	Stockholm University, Department of Ecology, Environment and Plant Sciences

APPENDIX 2: Sample preparation

The synthetic sample A1M was prepared by diluting from the NIST traceable certified reference materials produced by Inorganic Ventures. The synthetic sample A1Hg was prepared by diluting from the NIST traceable AccuTrace™ Reference Standard produced by AccuStandard, Inc. The water samples D2M and G3M were prepared by adding some separate metal solutions (Merck CertiPUR®) into the original water sample, if the original concentration was not high enough. Samples D2Hg and G3Hg were prepared by adding from the NIST traceable AccuTrace™ Reference Standard produced by AccuStandard, Inc., if the original concentration was not high enough.The tested sediment sample (after analysis: SC4, SN4, SO4) was reused sediment sample from the previous PT MET 04/2013 [4].

Measurand		A1M µg/l	D2M µg/l	G3M µg/l	SN4/SO4 mg/kg	Measurand		A1M µg/l	D2M µg/l	G3M µg/l	SN4/SO4 mg/kg
Al	Original	3350	19	15	22	Ni	Original	72.5	0.57	0.06	48
	Dilution	10	-	-	-		Dilution	10	-	-	-
	Addition	-	20	-	-		Addition	-	-	1.5	-
	Ass. value	335	37.9	14.3	22.4/25.9 g/kg		Ass. value	7.25	0.54	1.56	48.6/47.3
As	Original	12.5	0.41	0.18	6.6	N_{tot}	Original	-	-	-	2.9
	Dilution	10	-	-	-		Dilution	-	-	-	-
	Addition	-	-	-	-		Addition	-	-	-	-
	Ass. value	1.25	0.098	0.18	6.65/6.89		Ass. value	-	-	-	4.74/- g/kg
Cd	Original	7.5	0.004	0.005	0.78	Pb	Original	42.5	0.14	0.055	29
	Dilution	10	-	-	-		Dilution	10	-	-	-
	Addition	-	0.296	0.145	-		Addition	-	2	0.5	-
	Ass. value	0.75	0.31	0.15	0.73/0.69		Ass. value	4.24	2.18	0.57	28.7/25.8
Co	Original	22.5	0.03	0	33	P_{tot}	Original	-	-	-	1.2
	Dilution	10	-	-	-		Dilution	-	-	-	-
	Addition	-	0.3	0.2	-		Addition	-	-	-	-
	Ass. value	2.25	0.32	0.22	34.0/35.7		Ass. value	-	-	-	1.09/1.11 g/kg
Cr	Original	45	0.07	0.07	57	Se	Original	12.5	-	-	2.3
	Dilution	10	-	-	-		Dilution	10	-	-	-
	Addition	-	1.5	0.48	-		Addition	-	0.5	1.75	-
	Ass. value	4.50	1.57	0.54	56.3/58.9		Ass. value	1.25	0.52	1.90	2.60/2.81
Cu	Original	125	57	3.7	65	S_{tot}	Original	-	-	-	4.3
	Dilution	10	-	-	-		Dilution	-	-	-	-
	Addition	-	-	-	-		Addition	-	-	-	-
	Ass. value	12.5	56.8	3.57	68.1/70.2		Ass. value	-	-	-	4.37/4.00 g/kg
Fe	Original	1750	40	3.3	32	TC	Original	-	-	-	83.3
	Dilution	10	-	-	-		Dilution	-	-	-	-
	Addition	-	-	15	-		Addition	-	-	-	-
	Ass. value	175	37.5	17.5	32.9/34.5 g/kg		Ass. value	-	-	-	87.7 g/kg
Mn	Original	435	1.6	1.1	628	Ti	Original	225	0.1	-	1400
	Dilution	10	-	-	-		Dilution	10	-	-	-
	Addition	-	14	3	-		Addition	-	5	15	-
	Ass. value	43.5	15.6	4.01	630/702/		Ass. value	22.5	5.26	16.0	1800/1820
U	Original	6.5	0.12	2.4	3.6	Measurand		A1Hg µg/l	D2Hg µg/l	G3Hg µg/l	SC4/ SN4/ SO4 mg/kg
	Dilution	10	-	-	-						
	Addition	-	-	-	-						
	Ass. value	0.65	0.11	2.29	3.30/3.61						
V	Original	42.5	0.05	0.92	59	Hg	Original	-	-	-	0.74
	Dilution	10	-	-	-		Dilution	-	-	-	-
	Addition	-	3	-	-		Addition	0.15	0.075	0.05	-
	Ass. value	4.25	3.11	0.88	58.4/62.7		Ass. value	0.15	0.075	0.050	0.67/0.73/0.70
Zn	Original	335	10	1.3	207						
	Dilution	10	-	-	-						
	Addition	-	-	4	-						
	Ass. value	33.5	10.2	5.40	212/203						

Original = the original concentration; Dilution = the ratio of dilution; Addition = the addition concentration; Ass. value = the assigned value

APPENDIX 3: Homogeneity of the samples

The homogeneity was checked for the selected samples and measurands as duplicate measurements.

Criteria for homogeneity:

$s_{anal}/s_h<0.5$ and $s_{sam}^2<c$, where

s_h = standard deviation for testing of the homogeneity
s_{anal} = analytical deviation, standard deviation of the results in a sub sample
s_{sam} = between-sample deviation, standard deviation of the results between sub samples

$c = F1 \times s_{all}^2 + F2 \times s_{anal}^2$, where
$s_{all}^2 = (0.3 \times s_h)^2$,
F1 and F2 are constants of F distribution derived from the standard statistical tables for the tested number of samples [2, 3].

Measurand/Sample	Concentration [µg/l] [mg/kg]	n	s_{pt} %	s_h%	s_h	s_{anal}	s_{anal}/s_h	$s_{anal}/s_h<0.5$?	s_{sam}^2	c	$s_{sam}^2<c$?
Cd/D2M	0.32	3	7.5	0.9	0.003	0.001	0.463	Yes	0.000003	0.00001	Yes
Cr/D2M	1.64	3	7.5	1.7	0.028	0.003	0.124	Yes	0.00026	0.0003	Yes
Pb/D2M	2.18	3	7.5	0.6	0.013	0.006	0.446	Yes	0.00003	0.0002	Yes
Se/D2M	0.54	3	7.5	3.5	0.019	0.003	0.178	Yes	0.00014	0.00015	Yes
Zn/D2M	10.4	3	7.5	3.2	0.333	0.061	0.185	Yes	0.045	0.046	Yes
Cd/G3M	0.16	3	7.5	1.3	0.002	0.001	0.494	Yes	0.0000002	0.00001	Yes
Cr/G3M	0.55	3	7.5	2.2	0.012	0.006	0.485	Yes	0	0.0002	Yes
Pb/G3M	0.55	3	7.5	1.0	0.006	0.003	0.484	Yes	0	0.00004	Yes
Se/G3M	1.95	3	7.5	1.6	0.031	0.015	0.473	Yes	0	0.001	Yes
Zn/G3M	5.34	3	7.5	1.3	0.070	0.035	0.499	Yes	0	0.006	Yes
Cd/S4M	0.78	3	-	2.6	0.020	0.002	0.105	Yes	0.00012	0.00013	Yes
Cu/S4M	64.6	3	10	2.0	1.292	0.638	0.494	Yes	0	2.190	Yes
Hg/S4M	0.74	3	10	2.0	0.015	0.004	0.260	Yes	0.00012	0.00012	Yes
Mn/S4M	628	3	7.5	1.1	6.908	3.156	0.457	Yes	2.38	55.5	Yes
Zn/S4M	207	3	7.5	0.9	1.860	0.265	0.143	Yes	1.21	1.23	Yes
Hg/D2Hg*	0.07	3	12.5	1.0	0.0008	0.0004	0.466	Yes	0.0000002	0.000001	Yes
Hg/G3Hg*	0.05	3	12.5	0.5	0.0003	0.0001	0.486	Yes	0	0.0000001	Yes
Pb/D2M*	2.19	3	7.5	0.7	0.015	0.007	0.467	Yes	0.0001	0.0003	Yes
Pb/G3M*	0.57	3	7.5	0.4	0.002	0.0009	0.403	Yes	0.000001	0.000005	Yes

n= number of tested sub-samples
s_{pt} % = standard deviation for proficiency assessment
*) result based on the ID-ICP-MS measurement

Conclusion: The criteria were fulfilled for the tested measurands and the samples were regarded as homogenous

APPENDIX 4: Feedback from the proficiency test

FEEDBACK FROM THE PARTICIPANTS

Participant	Comments on technical execution	Action / Proftest SYKE
6	Participant informed receiving the samples two days after the estimated delivery day.	According to the distributor's tracking system the samples arrived to the participant on time. It is recommended to check the in-house process for sample delivery.
10	Participant received the samples one day after the estimated delivery day.	According to the distributor's tracking system the samples arrived to the participant on time. It is recommended to check the in-house process for sample delivery.

FEEDBACK TO THE PARTICIPANTS

Participant	Comments
12	The participant informed that they are accredited for Hg (A1Hg). However they did not report measurement uncertainty with their result. The measurement uncertainty should be reported with the results obtained by accredited method.
12	The participant reported lower than value for Co in the sample A1M, though the tested concentration was high enough to be measured. The provider recommends the participant to re-validate their limit of detection value.
3	The participant reported lower than value for Co in the sample A1M, though the tested concentration was high enough to be measured. The provider recommends the participant to re-validate their limit of detection value.

APPENDIX 5: Evaluation of the assigned values and their uncertainties

Measurand	Sample	Unit	Assigned value	U_{pt}	U_{pt}, %	Evaluation method of assigned value	u_{pt}/S_{pt}
Al	A1M	µg/l	335	2	0.5	Calculated value	0.05
	D2M	µg/l	37.9	1.4	3.8	Robust mean	0.25
	G3M	µg/l	14.3	0.9	6.0	Robust mean	0.30
	SN4	g/kg	22.4	4.5	20.0	Median	
	SO4	g/kg	25.9	2.8	11.0	Median	0.44
As	A1M	µg/l	1.25	0.01	0.7	Calculated value	0.05
	D2M	µg/l	0.098	0.005	5.6	Median	0.28
	G3M	µg/l	0.18	0.01	3.5	Median	0.18
	SN4	mg/kg	6.65	0.62	9.3	Median	
	SO4	mg/kg	6.89	0.76	11.0	Median	0.44
Cd	A1M	µg/l	0.75	0.01	0.7	Calculated value	0.05
	D2M	µg/l	0.31	0.01	3.7	Robust mean	0.25
	G3M	µg/l	0.15	0.01	4.0	Median	0.27
	SN4	mg/kg	0.73	0.11	15.0	Median	
	SO4	mg/kg	0.69	0.09	13.0	Median	
Co	A1M	µg/l	2.25	0.01	0.6	Calculated value	0.06
	D2M	µg/l	0.32	0.02	4.8	Median	0.32
	G3M	µg/l	0.22	0.01	2.6	Median	0.17
	SN4	mg/kg	34.0	1.9	5.6	Median	
	SO4	mg/kg	35.7	2.1	6.0	Median	0.30
Cr	A1M	µg/l	4.50	0.03	0.7	Calculated value	0.05
	D2M	µg/l	1.57	0.04	2.3	Median	0.15
	G3M	µg/l	0.54	0.02	3.4	Median	0.23
	SN4	mg/kg	56.3	4.1	7.2	Median	0.29
	SO4	mg/kg	58.9	4.9	8.4	Median	0.34
Cu	A1M	µg/l	12.5	0.1	0.4	Calculated value	0.04
	D2M	µg/l	56.8	2.1	3.7	Robust mean	0.25
	G3M	µg/l	3.57	0.20	5.6	Robust mean	0.28
	SN4	mg/kg	68.1	2.9	4.2	Median	0.21
	SO4	mg/kg	70.2	2.7	3.8	Median	0.19
Drw	S4M	%	98.1	0.3	0.3	Median	0.06
Fe	A1M	µg/l	175	1	0.6	Calculated value	0.06
	D2M	µg/l	37.5	2.1	5.5	Robust mean	0.37
	G3M	µg/l	17.5	1.1	6.5	Robust mean	0.33
	SN4	g/kg	32.9	3.0	9.2	Median	0.46
	SO4	g/kg	34.5	2.2	6.3	Median	0.32
Hg	A1Hg	µg/l	0.15	0.00	3.0	ID-ICP-MS	0.15
	D2Hg	µg/l	0.075	0.002	3.0	ID-ICP-MS	0.12
	G3Hg	µg/l	0.050	0.002	3.0	ID-ICP-MS	0.12
	SC4	mg/kg	0.67			Median	
	SN4	mg/kg	0.73	0.03	3.7	Median	
	SO4	mg/kg	0.70	0.05	7.1	Median	0.36
Mn	A1M	µg/l	43.5	0.3	0.6	Calculated value	0.06
	D2M	µg/l	15.6	0.7	4.4	Robust mean	0.29
	G3M	µg/l	4.01	0.16	3.9	Robust mean	0.26
	SN4	mg/kg	630	30	4.7	Median	0.31
	SO4	mg/kg	702	25	3.5	Median	0.23

Measurand	Sample	Unit	Assigned value	U_{pt}	U_{pt}, %	Evaluation method of assigned value	u_{pt}/s_{pt}
Ni	A1M	µg/l	7.25	0.04	0.6	Calculated value	0.04
	D2M	µg/l	0.54	0.01	1.5	Median	0.08
	G3M	µg/l	1.56	0.05	3.5	Median	0.23
	SN4	mg/kg	48.6	2.4	5.0	Median	
	SO4	mg/kg	47.3	3.4	7.1	Median	0.36
N_{tot}	SN4	g/kg	4.74	0.24	5.0	Median	
	SO4	g/kg					
Pb	A1M	µg/l	4.24	0.11	2.5	ID-ICP-MS	0.17
	D2M	µg/l	2.18	0.05	2.5	ID-ICP-MS	0.17
	G3M	µg/l	0.57	0.03	4.4	ID-ICP-MS	0.29
	SN4	mg/kg	28.7	1.7	6.0	Median	
	SO4	mg/kg	25.8	2.5	9.5	Median	0.38
P_{tot}	SN4	g/kg	1.09	0.08	7.6	Median	0.38
	SO4	g/kg	1.11	0.08	7.4	Median	0.37
Se	A1M	µg/l	1.25	0.01	0.7	Calculated value	0.05
	D2M	µg/l	0.52	0.02	3.5	Median	0.23
	G3M	µg/l	1.90	0.03	1.6	Median	0.11
	SN4	mg/kg	2.60	0.62	24.0	Median	
	SO4	mg/kg	2.81			Median	
S_{tot}	SN4	g/kg	4.37	0.48	11.0	Median	
	SO4	g/kg	4.00	0.37	9.3	Median	
TC	S4M	g/kg	87.7	5.5	6.3	Median	
Ti	A1M	µg/l	22.5	0.2	0.7	Calculated value	0.07
	D2M	µg/l	5.26	0.22	4.1	Median	0.27
	G3M	µg/l	16.0	0.7	4.2	Median	0.28
	SN4	mg/kg	1800			Median	
	SO4	mg/kg	1820			Median	
U	A1M	µg/l	0.65	0.00	0.6	Calculated value	0.04
	D2M	µg/l	0.11	0.01	8.2	Median	0.33
	G3M	µg/l	2.29	0.08	3.6	Median	0.24
	SN4	mg/kg	3.30	0.29	8.8	Median	
	SO4	mg/kg	3.61	0.72	20.0	Median	
V	A1M	µg/l	4.25	0.03	0.6	Calculated value	0.06
	D2M	µg/l	3.11	0.09	3.0	Median	0.20
	G3M	µg/l	0.88	0.04	4.8	Median	0.32
	SN4	mg/kg	58.4	5.8	9.9	Median	
	SO4	mg/kg	62.7	5.4	8.6	Median	
Zn	A1M	µg/l	33.5	0.2	0.6	Calculated value	0.06
	D2M	µg/l	10.2	0.3	3.2	Robust mean	0.21
	G3M	µg/l	5.40	0.26	4.9	Robust mean	0.33
	SN4	mg/kg	212	6	2.7	Median	0.18
	SO4	mg/kg	203	10	4.9	Median	

U_{pt} = Expanded uncertainty of the assigned value
Criterion for reliability of the assigned value $u_{pt}/s_{pt} \leq 0.3$, where
s_{pt}= the standard deviation for proficiency assessment
u_{pt}= the standard uncertainty of the assigned value

If $u_{pt}/s_{pt} \leq 0.3$, the assigned value is reliable and the z scores are qualified.

APPENDIX 6: Terms in the results tables

Results of each participant

Measurand	The tested parameter
Sample	The code of the sample
z score	Calculated as follows: $z = (x_i - x_{pt})/s_{pt}$, where x_i = the result of the individual participant x_{pt} = the assigned value s_{pt} = the standard deviation for proficiency assessment
Assigned value	The value attributed to a particular property of a proficiency test item
2 × s_{pt} %	The standard deviation for proficiency assessment (s_{pt}) at the 95 % confidence level
Participant's result	The result reported by the participant (the mean value of the replicates)
Md	Median
s	Standard deviation
s %	Standard deviation, %
n_{stat}	Number of results in statistical processing

Summary on the z scores

S – satisfactory ($-2 \le z \le 2$)
Q – questionable ($2 < z < 3$), positive error, the result deviates more than 2 × s_{pt} from the assigned value
q – questionable ($-3 < z < -2$), negative error, the result deviates more than 2 × s_{pt} from the assigned value
U – unsatisfactory ($z \ge 3$), positive error, the result deviates more than 3 × s_{pt} from the assigned value
u – unsatisfactory ($z \le -3$), negative error, the result deviates more than 3 × s_{pt} from the assigned value

Robust analysis

The items of data are sorted into increasing order, $x_1, x_2, x_i, \ldots, x_p$.
Initial values for x^* and s^* are calculated as:
x^* = median of x_i (i = 1, 2, ...,p)
s^* = 1.483 × median of $|x_i - x^*|$ (i = 1, 2, ...,p)

The mean x^* and s^* are updated as follows:
Calculate $\varphi = 1.5 \times s^*$. A new value is then calculated for each result x_i ($i = 1, 2 \ldots p$):

$$x_i^* = \begin{cases} x^* - \varphi, & \text{if } x_i < x^* - \varphi \\ x^* + \varphi, & \text{if } x_i > x^* + \varphi, \\ x_i & \text{otherwise} \end{cases}$$

The new values of x^* and s^* are calculated from:

$$x^* = \sum x_i^* / p$$

$$s^* = 1.134\sqrt{\sum (x_i^* - x^*)^2 / (p-1)}$$

The robust estimates x^* and s^* can be derived by an iterative calculation, i.e. by updating the values of x^* and s^* several times, until the process convergences [2].

APPENDIX 7: Results of each participant

Participant 1												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	s	s %	n_{stat}
Al	µg/l	A1M		-0.18	335	10	332	332	331	22	6.7	16
	µg/l	D2M		-0.35	37.9	15	36.9	37.6	37.9	1.5	4.0	14
	µg/l	G3M		0.07	14.3	20	14.4	14.2	14.4	1.2	8.6	12
	g/kg	SO4		-0.17	25.9	25	25.4	25.9	25.1	3.3	13.0	6
As	µg/l	A1M		-0.21	1.25	15	1.23	1.21	1.22	0.06	5.3	10
	µg/l	D2M			0.098	20	*< 0.5*	0.098	0.098	0.008	8.4	9
	µg/l	G3M			0.18	20	*< 0.5*	0.18	0.18	0.01	4.6	7
	mg/kg	SO4		-0.88	6.89	25	6.13	6.89	6.82	0.95	14.0	6
Cd	µg/l	A1M		0.18	0.75	15	0.76	0.74	0.73	0.05	6.7	12
	µg/l	D2M		-0.43	0.31	15	0.30	0.31	0.31	0.02	6.5	12
	µg/l	G3M		5.33	0.15	15	0.21	0.15	0.15	0.01	6.3	10
	mg/kg	SO4			0.69		0.50	0.69	0.67	0.11	16.3	6
Co	µg/l	A1M		-1.07	2.25	10	2.13	2.17	2.17	0.07	3.4	11
	µg/l	D2M		-0.83	0.32	15	0.30	0.32	0.32	0.02	6.8	9
	µg/l	G3M			0.22	15	*< 0.3*	0.22	0.22	0.01	3.4	7
	mg/kg	SO4		-0.06	35.7	20	35.5	35.7	35.1	2.6	7.3	6
Cr	µg/l	A1M		-0.59	4.50	15	4.30	4.40	4.40	0.22	5.0	13
	µg/l	D2M		-0.59	1.57	15	1.50	1.57	1.56	0.06	3.6	10
	µg/l	G3M			0.54	15	*<1*	0.54	0.55	0.03	5.2	9
	mg/kg	SO4		-0.57	58.9	25	54.7	58.9	58.9	6.1	10.3	6
Cu	µg/l	A1M		-0.64	12.5	10	12.1	12.1	12.0	1.0	8.2	15
	µg/l	D2M		-0.77	56.8	15	53.5	55.8	56.9	2.9	5.2	14
	µg/l	G3M		-0.48	3.57	20	3.40	3.51	3.55	0.27	7.6	12
	mg/kg	SO4		0.06	70.2	20	70.6	70.2	69.0	3.2	4.6	6
Drw	%	S4M		0.77	98.1	5	100.0	98.1	98.0	0.5	0.5	10
Fe	µg/l	A1M		0.57	175	10	180	173	176	8	4.7	15
	µg/l	D2M		-1.00	37.5	15	34.7	37.1	37.7	3.2	8.6	14
	µg/l	G3M		-0.51	17.5	20	16.6	17.4	17.6	1.6	8.9	12
	g/kg	SO4		-0.81	34.5	20	31.7	34.5	34.6	2.7	7.7	6
Hg	µg/l	A1Hg		-1.33	0.15	20	0.13	0.16	0.15	0.02	9.8	10
	µg/l	D2Hg			0.075	25	*< 0.13*	0.075	0.074	0.006	8.0	7
	µg/l	G3Hg			0.050	25	*< 0.13*	0.054	0.053	0.009	16.3	8
	mg/kg	SO4		-3.86	0.70	20	0.43	0.70	0.71	0.06	8.7	6
Mn	µg/l	A1M		0.23	43.5	10	44.0	43.7	43.5	2.0	4.5	15
	µg/l	D2M		-0.26	15.6	15	15.3	15.9	15.8	0.7	4.6	15
	µg/l	G3M		-0.03	4.01	15	4.00	4.02	4.02	0.23	5.7	12
	mg/kg	SO4		-0.47	702	15	677	702	705	31	4.3	6
Ni	µg/l	A1M		0.09	7.25	15	7.30	7.20	7.18	0.34	4.8	12
	µg/l	D2M			0.54	20	*<1*	0.54	0.55	0.01	2.0	7
	µg/l	G3M		0.00	1.56	15	1.56	1.56	1.55	0.08	5.3	9
	mg/kg	SO4		-1.18	47.3	20	41.7	47.3	47.7	4.1	8.6	6
N_{tot}	g/kg	SN4			4.74		4.90	4.74	4.62	0.26	5.6	5
Pb	µg/l	A1M		-0.13	4.24	15	4.20	4.20	4.19	0.15	3.6	12
	µg/l	D2M		-1.10	2.18	15	2.00	2.18	2.13	0.12	5.6	12
	µg/l	G3M		-0.94	0.57	15	0.53	0.56	0.56	0.04	7.6	11
	mg/kg	SO4		-1.21	25.8	25	21.9	25.8	26.0	3.0	11.7	6

Participant 1												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	s	s %	n_{stat}
P_{tot}	g/kg	SO4		-0.05	1.11	20	1.11	1.11	1.12	0.10	9.1	6
Se	µg/l	A1M		0.43	1.25	15	1.29	1.21	1.22	0.13	10.7	10
	µg/l	D2M			0.52	15	*<1*	0.52	0.53	0.03	5.3	9
	µg/l	G3M		0.00	1.90	15	1.90	1.90	1.92	0.04	2.3	8
	mg/kg	SO4			2.81		1.01	2.81	3.04	1.88	61.8	4
S_{tot}	g/kg	SO4			4.00		3.74	3.99	4.08	0.38	9.3	4
TC	g/kg	S4M			87.7		95.4	87.7	87.3	6.1	7.0	5
Ti	µg/l	A1M		0.80	22.5	10	23.4	21.6	21.7	0.9	4.0	9
	µg/l	D2M			5.26	15	*<10*	5.26	5.30	0.29	5.4	7
	µg/l	G3M		1.33	16.0	15	17.6	16.0	16.1	0.9	5.9	8
	mg/kg	SO4			1820		2184	1820	1758	460	26.2	3
U	µg/l	A1M		-0.82	0.65	15	0.61	0.65	0.63	0.03	5.0	11
	µg/l	D2M			0.11	25	*<0,5*	0.11	0.11	0.01	13.6	11
	µg/l	G3M		-0.87	2.29	15	2.14	2.29	2.28	0.14	6.0	11
	mg/kg	SO4			3.61		3.61	3.61	3.39	0.59	17.4	3
V	µg/l	A1M		-1.74	4.25	10	3.88	4.03	4.05	0.14	3.3	11
	µg/l	D2M		-1.33	3.11	15	2.80	3.11	3.06	0.15	5.0	11
	µg/l	G3M		-1.06	0.88	15	0.81	0.88	0.88	0.06	7.1	9
	mg/kg	SO4			62.7		60.4	62.7	61.4	6.5	10.6	6
Zn	µg/l	A1M		1.37	33.5	10	35.8	33.0	33.0	1.6	5.0	13
	µg/l	D2M		-0.41	10.2	15	9.9	10.2	10.2	0.4	3.9	12
	µg/l	G3M		-0.42	5.40	15	5.23	5.22	5.35	0.29	5.3	12
	mg/kg	SO4			203		200	203	208	11	5.5	5

Participant 2												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	s	s %	n_{stat}
U	µg/l	A1M		-0.10	0.65	15	0.65	0.65	0.63	0.03	5.0	11
	µg/l	D2M		0.15	0.11	25	0.11	0.11	0.11	0.01	13.6	11
	µg/l	G3M		0.35	2.29	15	2.35	2.29	2.28	0.14	6.0	11
	mg/kg	SN4			3.30		2.77	3.30	3.27	0.32	9.8	5

Participant 3												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	s	s %	n_{stat}
Al	µg/l	A1M		2.21	335	10	372	332	331	22	6.7	16
	µg/l	D2M			37.9	15	*<100*	37.6	37.9	1.5	4.0	14
	µg/l	G3M			14.3	20	*<100*	14.2	14.4	1.2	8.6	12
	g/kg	SO4		0.65	25.9	25	28.0	25.9	25.1	3.3	13.0	6
As	µg/l	A1M			1.25	15	*< 10.0*	1.21	1.22	0.06	5.3	10
	µg/l	D2M			0.098	20	*<10*	0.098	0.098	0.008	8.4	9
	µg/l	G3M			0.18	20	*<10*	0.18	0.18	0.01	4.6	7
	mg/kg	SO4		0.01	6.89	25	6.90	6.89	6.82	0.95	14.0	6
Cd	µg/l	A1M			0.75	15	*< 1.00*	0.74	0.73	0.05	6.7	12
	µg/l	D2M			0.31	15	*< 1.00*	0.31	0.31	0.02	6.5	12
	µg/l	G3M			0.15	15	*< 1.00*	0.15	0.15	0.01	6.3	10
	mg/kg	SO4			0.69		0.65	0.69	0.67	0.11	16.3	6

Participant 3												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	s	s %	n_{stat}
Co	µg/l	A1M		9.87	2.25	10	3.36	2.17	2.17	0.07	3.4	11
	µg/l	D2M			0.32	15	*< 1.00*	0.32	0.32	0.02	6.8	9
	µg/l	G3M			0.22	15	*< 1.00*	0.22	0.22	0.01	3.4	7
	mg/kg	SO4		0.36	35.7	20	37.0	35.7	35.1	2.6	7.3	6
Cr	µg/l	A1M			4.50	15	*< 5.00*	4.40	4.40	0.22	5.0	13
	µg/l	D2M			1.57	15	*< 5.00*	1.57	1.56	0.06	3.6	10
	µg/l	G3M			0.54	15	*< 5.00*	0.54	0.55	0.03	5.2	9
	mg/kg	SO4		0.01	58.9	25	59.0	58.9	58.9	6.1	10.3	6
Cu	µg/l	A1M		1.60	12.5	10	13.5	12.1	12.0	1.0	8.2	15
	µg/l	D2M		1.36	56.8	15	62.6	55.8	56.9	2.9	5.2	14
	µg/l	G3M			3.57	20	*< 5.00*	3.51	3.55	0.27	7.6	12
	mg/kg	SO4		0.26	70.2	20	72.0	70.2	69.0	3.2	4.6	6
Drw	%	S4M		-0.20	98.1	5	97.6	98.1	98.0	0.5	0.5	10
Fe	µg/l	A1M		1.03	175	10	184	173	176	8	4.7	15
	µg/l	D2M		0.04	37.5	15	37.6	37.1	37.7	3.2	8.6	14
	µg/l	G3M		-0.57	17.5	20	16.5	17.4	17.6	1.6	8.9	12
	g/kg	SO4		1.01	34.5	20	38.0	34.5	34.6	2.7	7.7	6
Hg	µg/l	A1Hg		-3.07	0.15	20	0.10	0.16	0.15	0.02	9.8	10
	µg/l	D2Hg			0.075	25	*< 0.10*	0.075	0.074	0.006	8.0	7
	µg/l	G3Hg			0.050	25	*< 0.10*	0.054	0.053	0.009	16.3	8
	mg/kg	SO4		-0.16	0.70	20	0.69	0.70	0.71	0.06	8.7	6
Mn	µg/l	A1M		1.15	43.5	10	46.0	43.7	43.5	2.0	4.5	15
	µg/l	D2M		0.60	15.6	15	16.3	15.9	15.8	0.7	4.6	15
	µg/l	G3M			4.01	15	*< 5.00*	4.02	4.02	0.23	5.7	12
	mg/kg	SO4		0.72	702	15	740	702	705	31	4.3	6
Ni	µg/l	A1M		1.10	7.25	15	7.85	7.20	7.18	0.34	4.8	12
	µg/l	D2M			0.54	20	*< 5.00*	0.54	0.55	0.01	2.0	7
	µg/l	G3M			1.56	15	*< 5.00*	1.56	1.55	0.08	5.3	9
	mg/kg	SO4		-0.06	47.3	20	47.0	47.3	47.7	4.1	8.6	6
Pb	µg/l	A1M			4.24	15	*< 10.0*	4.20	4.19	0.15	3.6	12
	µg/l	D2M			2.18	15	*< 10.0*	2.18	2.13	0.12	5.6	12
	µg/l	G3M			0.57	15	*< 10.0*	0.56	0.56	0.04	7.6	11
	mg/kg	SO4		-0.56	25.8	25	24.0	25.8	26.0	3.0	11.7	6
P_{tot}	g/kg	SO4		1.71	1.11	20	1.30	1.11	1.12	0.10	9.1	6
Se	µg/l	A1M			1.25	15	*< 10.0*	1.21	1.22	0.13	10.7	10
	µg/l	D2M			0.52	15	*< 10.0*	0.52	0.53	0.03	5.3	9
	µg/l	G3M			1.90	15	*< 10.00*	1.90	1.92	0.04	2.3	8
	mg/kg	SO4			2.81		*< 1.0*	2.81	3.04	1.88	61.8	4
S_{tot}	g/kg	SO4			4.00		*< 0.1*	3.99	4.08	0.38	9.3	4
TC	g/kg	S4M			87.7		90.0	87.7	87.3	6.1	7.0	5
V	µg/l	A1M			4.25	10	*< 10.0*	4.03	4.05	0.14	3.3	11
	µg/l	D2M			3.11	15	*< 10.0*	3.11	3.06	0.15	5.0	11
	µg/l	G3M			0.88	15	*< 10.00*	0.88	0.88	0.06	7.1	9
	mg/kg	SO4			62.7		64.0	62.7	61.4	6.5	10.6	6
Zn	µg/l	A1M		0.06	33.5	10	33.6	33.0	33.0	1.6	5.0	13
	µg/l	D2M		-0.26	10.2	15	10.0	10.2	10.2	0.4	3.9	12
	µg/l	G3M		-0.10	5.40	15	5.36	5.22	5.35	0.29	5.3	12
	mg/kg	SO4			203		200	203	208	11	5.5	5

Participant 4												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	$2\times s_{pt}$ %	Participant's result	Md	Mean	s	s %	n_{stat}
Al	µg/l	A1M		-1.85	335	10	304	332	331	22	6.7	16
	µg/l	D2M		-0.49	37.9	15	36.5	37.6	37.9	1.5	4.0	14
	µg/l	G3M		-0.63	14.3	20	13.4	14.2	14.4	1.2	8.6	12
	g/kg	SO4		-2.07	25.9	25	19.2	25.9	25.1	3.3	13.0	6
As	µg/l	A1M		-1.17	1.25	15	1.14	1.21	1.22	0.06	5.3	10
	µg/l	D2M		0.51	0.098	20	0.103	0.098	0.098	0.008	8.4	9
	µg/l	G3M		-2.61	0.18	20	0.13	0.18	0.18	0.01	4.6	7
	mg/kg	SO4		0.92	6.89	25	7.68	6.89	6.82	0.95	14.0	6
Cd	µg/l	A1M		-0.76	0.75	15	0.71	0.74	0.73	0.05	6.7	12
	µg/l	D2M		-0.30	0.31	15	0.30	0.31	0.31	0.02	6.5	12
	µg/l	G3M		0.44	0.15	15	0.16	0.15	0.15	0.01	6.3	10
	mg/kg	SO4			0.69		0.73	0.69	0.67	0.11	16.3	6
Co	µg/l	A1M		-1.51	2.25	10	2.08	2.17	2.17	0.07	3.4	11
	µg/l	D2M		-0.21	0.32	15	0.32	0.32	0.32	0.02	6.8	9
	µg/l	G3M		0.42	0.22	15	0.23	0.22	0.22	0.01	3.4	7
	mg/kg	SO4		-1.43	35.7	20	30.6	35.7	35.1	2.6	7.3	6
Cr	µg/l	A1M		-0.80	4.50	15	4.23	4.40	4.40	0.22	5.0	13
	µg/l	D2M		0.17	1.57	15	1.59	1.57	1.56	0.06	3.6	10
	µg/l	G3M		-0.42	0.54	15	0.52	0.54	0.55	0.03	5.2	9
	mg/kg	SO4		-1.22	58.9	25	49.9	58.9	58.9	6.1	10.3	6
Cu	µg/l	A1M		-3.20	12.5	10	10.5	12.1	12.0	1.0	8.2	15
	µg/l	D2M		-0.26	56.8	15	55.7	55.8	56.9	2.9	5.2	14
	µg/l	G3M		0.34	3.57	20	3.69	3.51	3.55	0.27	7.6	12
	mg/kg	SO4		-0.34	70.2	20	67.8	70.2	69.0	3.2	4.6	6
Drw	%	S4M		-0.09	98.1	5	97.9	98.1	98.0	0.5	0.5	10
Fe	µg/l	A1M		-0.46	175	10	171	173	176	8	4.7	15
	µg/l	D2M		-0.39	37.5	15	36.4	37.1	37.7	3.2	8.6	14
	µg/l	G3M		-0.34	17.5	20	16.9	17.4	17.6	1.6	8.9	12
	g/kg	SO4		-0.72	34.5	20	32.0	34.5	34.6	2.7	7.7	6
Hg	µg/l	A1Hg		0.73	0.15	20	0.16	0.16	0.15	0.02	9.8	10
	µg/l	D2Hg		2.45	0.075	25	0.098	0.075	0.074	0.006	8.0	7
	µg/l	G3Hg		4.32	0.050	25	0.077	0.054	0.053	0.009	16.3	8
	mg/kg	SO4		-0.90	0.70	20	0.64	0.70	0.71	0.06	8.7	6
Mn	µg/l	A1M		-1.52	43.5	10	40.2	43.7	43.5	2.0	4.5	15
	µg/l	D2M		-3.25	15.6	15	11.8	15.9	15.8	0.7	4.6	15
	µg/l	G3M		0.00	4.01	15	4.01	4.02	4.02	0.23	5.7	12
	mg/kg	SO4		-0.57	702	15	672	702	705	31	4.3	6
Ni	µg/l	A1M		-0.99	7.25	15	6.71	7.20	7.18	0.34	4.8	12
	µg/l	D2M		-0.22	0.54	20	0.53	0.54	0.55	0.01	2.0	7
	µg/l	G3M		3.76	1.56	15	2.00	1.56	1.55	0.08	5.3	9
	mg/kg	SO4		-0.25	47.3	20	46.1	47.3	47.7	4.1	8.6	6
N_{tot}	g/kg	SO4					4.83	4.83	4.83	0.00	0.0	1
Pb	µg/l	A1M		-0.22	4.24	15	4.17	4.20	4.19	0.15	3.6	12
	µg/l	D2M		-0.06	2.18	15	2.17	2.18	2.13	0.12	5.6	12
	µg/l	G3M		0.07	0.57	15	0.57	0.56	0.56	0.04	7.6	11
	mg/kg	SO4		-0.31	25.8	25	24.8	25.8	26.0	3.0	11.7	6
P_{tot}	g/kg	SO4		-0.63	1.11	20	1.04	1.11	1.12	0.10	9.1	6

Participant 4												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	s	s %	n_{stat}
Se	µg/l	A1M		-1.17	1.25	15	1.14	1.21	1.22	0.13	10.7	10
	µg/l	D2M		0.62	0.52	15	0.54	0.52	0.53	0.03	5.3	9
	µg/l	G3M		0.00	1.90	15	1.90	1.90	1.92	0.04	2.3	8
	mg/kg	SO4			2.81		3.07	2.81	3.04	1.88	61.8	4
S_{tot}	g/kg	SO4			4.00		4.04	3.99	4.08	0.38	9.3	4
TC	g/kg	S4M			87.7		79.1	87.7	87.3	6.1	7.0	5
Ti	µg/l	A1M		-1.33	22.5	10	21.0	21.6	21.7	0.9	4.0	9
	µg/l	D2M		-0.23	5.26	15	5.17	5.26	5.30	0.29	5.4	7
	µg/l	G3M		-0.50	16.0	15	15.4	16.0	16.1	0.9	5.9	8
	mg/kg	SO4			1820		1270	1820	1758	460	26.2	3
U	µg/l	A1M		0.43	0.65	15	0.67	0.65	0.63	0.03	5.0	11
	µg/l	D2M		0.58	0.11	25	0.12	0.11	0.11	0.01	13.6	11
	µg/l	G3M		0.82	2.29	15	2.43	2.29	2.28	0.14	6.0	11
V	µg/l	A1M		-1.51	4.25	10	3.93	4.03	4.05	0.14	3.3	11
	µg/l	D2M		-0.09	3.11	15	3.09	3.11	3.06	0.15	5.0	11
	µg/l	G3M		1.82	0.88	15	1.00	0.88	0.88	0.06	7.1	9
	mg/kg	SO4			62.7		49.5	62.7	61.4	6.5	10.6	6
Zn	µg/l	A1M		-6.63	33.5	10	22.4	33.0	33.0	1.6	5.0	13
	µg/l	D2M		0.13	10.2	15	10.3	10.2	10.2	0.4	3.9	12
	µg/l	G3M		0.99	5.40	15	5.80	5.22	5.35	0.29	5.3	12

Participant 5												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	s	s %	n_{stat}
Al	µg/l	A1M		0.24	335	10	339	332	331	22	6.7	16
	µg/l	D2M		0.32	37.9	15	38.8	37.6	37.9	1.5	4.0	14
	µg/l	G3M		-0.07	14.3	20	14.2	14.2	14.4	1.2	8.6	12
	g/kg	SN4			22.4		22.9	22.4	20.8	4.1	19.9	4
	g/kg	SO4		0.19	25.9	25	26.5	25.9	25.1	3.3	13.0	6
As	µg/l	A1M		-0.21	1.25	15	1.23	1.21	1.22	0.06	5.3	10
	µg/l	D2M		0.51	0.098	20	0.103	0.098	0.098	0.008	8.4	9
	µg/l	G3M		0.61	0.18	20	0.19	0.18	0.18	0.01	4.6	7
	mg/kg	SN4			6.65		6.65	6.65	6.36	0.66	10.4	5
	mg/kg	SO4		-0.02	6.89	25	6.87	6.89	6.82	0.95	14.0	6
Cd	µg/l	A1M		0.11	0.75	15	0.76	0.74	0.73	0.05	6.7	12
	µg/l	D2M		0.30	0.31	15	0.32	0.31	0.31	0.02	6.5	12
	µg/l	G3M		1.07	0.15	15	0.16	0.15	0.15	0.01	6.3	10
	mg/kg	SN4			0.73		0.78	0.73	0.77	0.13	16.3	5
	mg/kg	SO4			0.69		0.78	0.69	0.67	0.11	16.3	6
Co	µg/l	A1M		0.27	2.25	10	2.28	2.17	2.17	0.07	3.4	11
	µg/l	D2M		0.17	0.32	15	0.32	0.32	0.32	0.02	6.8	9
	µg/l	G3M		-1.03	0.22	15	0.20	0.22	0.22	0.01	3.4	7
	mg/kg	SN4			34.0		34.0	34.0	34.0	2.1	6.2	5
	mg/kg	SO4		0.53	35.7	20	37.6	35.7	35.1	2.6	7.3	6
Cr	µg/l	A1M		0.18	4.50	15	4.56	4.40	4.40	0.22	5.0	13
	µg/l	D2M		0.25	1.57	15	1.60	1.57	1.56	0.06	3.6	10
	µg/l	G3M		0.05	0.54	15	0.54	0.54	0.55	0.03	5.2	9
	mg/kg	SN4		0.31	56.3	25	58.5	56.3	55.3	4.9	8.9	6
	mg/kg	SO4		1.06	58.9	25	66.7	58.9	58.9	6.1	10.3	6

Participant 5												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	s	s %	n_{stat}
Cu	µg/l	A1M		0.16	12.5	10	12.6	12.1	12.0	1.0	8.2	15
	µg/l	D2M		-0.38	56.8	15	55.2	55.8	56.9	2.9	5.2	14
	µg/l	G3M		-0.25	3.57	20	3.48	3.51	3.55	0.27	7.6	12
	mg/kg	SN4		-0.51	68.1	20	64.6	68.1	66.4	3.4	5.2	6
	mg/kg	SO4		0.10	70.2	20	70.9	70.2	69.0	3.2	4.6	6
Drw	%	S4M		-0.33	98.1	5	97.3	98.1	98.0	0.5	0.5	10
Fe	µg/l	A1M		0.34	175	10	178	173	176	8	4.7	15
	µg/l	D2M		-0.36	37.5	15	36.5	37.1	37.7	3.2	8.6	14
	µg/l	G3M		-0.91	17.5	20	15.9	17.4	17.6	1.6	8.9	12
	g/kg	SN4		-0.40	32.9	20	31.6	32.9	33.1	3.7	11.3	6
	g/kg	SO4		0.70	34.5	20	36.9	34.5	34.6	2.7	7.7	6
Hg	µg/l	A1Hg		0.53	0.15	20	0.16	0.16	0.15	0.02	9.8	10
	µg/l	D2Hg		0.16	0.075	25	0.077	0.075	0.074	0.006	8.0	7
	µg/l	G3Hg		0.42	0.050	25	0.053	0.054	0.053	0.009	16.3	8
	mg/kg	SN4			0.73		0.73	0.73	0.73	0.03	4.1	5
	mg/kg	SO4		0.60	0.70	20	0.74	0.70	0.71	0.06	8.7	6
Mn	µg/l	A1M		0.64	43.5	10	44.9	43.7	43.5	2.0	4.5	15
	µg/l	D2M		0.26	15.6	15	15.9	15.9	15.8	0.7	4.6	15
	µg/l	G3M		-0.40	4.01	15	3.89	4.02	4.02	0.23	5.7	12
	mg/kg	SN4		0.08	630	15	634	630	639	37	5.7	6
	mg/kg	SO4		0.68	702	15	738	702	705	31	4.3	6
Ni	µg/l	A1M		0.17	7.25	15	7.34	7.20	7.18	0.34	4.8	12
	µg/l	D2M		0.19	0.54	20	0.55	0.54	0.55	0.01	2.0	7
	µg/l	G3M		-0.60	1.56	15	1.49	1.56	1.55	0.08	5.3	9
	mg/kg	SN4			48.6		48.9	48.6	47.3	2.7	5.6	5
	mg/kg	SO4		1.46	47.3	20	54.2	47.3	47.7	4.1	8.6	6
Pb	µg/l	A1M		0.25	4.24	15	4.32	4.20	4.19	0.15	3.6	12
	µg/l	D2M		0.12	2.18	15	2.20	2.18	2.13	0.12	5.6	12
	µg/l	G3M		-0.21	0.57	15	0.56	0.56	0.56	0.04	7.6	11
	mg/kg	SN4			28.7		28.7	28.7	28.5	1.9	6.7	5
	mg/kg	SO4		1.43	25.8	25	30.4	25.8	26.0	3.0	11.7	6
P_{tot}	g/kg	SN4		-0.73	1.09	20	1.01	1.09	1.10	0.11	10.1	7
Se	µg/l	A1M		-0.43	1.25	15	1.21	1.21	1.22	0.13	10.7	10
	µg/l	D2M		0.26	0.52	15	0.53	0.52	0.53	0.03	5.3	9
	µg/l	G3M		0.49	1.90	15	1.97	1.90	1.92	0.04	2.3	8
	mg/kg	SN4			2.60		2.55	2.60	2.66	0.80	30.0	6
	mg/kg	SO4			2.81		2.54	2.81	3.04	1.88	61.8	4
S_{tot}	g/kg	SN4			4.37		3.59	4.37	4.25	0.47	11.1	4
Ti	µg/l	A1M		0.09	22.5	10	22.6	21.6	21.7	0.9	4.0	9
	µg/l	D2M		0.00	5.26	15	5.26	5.26	5.30	0.29	5.4	7
	µg/l	G3M		-0.17	16.0	15	15.8	16.0	16.1	0.9	5.9	8
	mg/kg	SN4			1800		1400	1800	1681	244	14.5	3
	mg/kg	SO4			1820		1820	1820	1758	460	26.2	3
U	µg/l	A1M		0.04	0.65	15	0.65	0.65	0.63	0.03	5.0	11
	µg/l	D2M		0.07	0.11	25	0.11	0.11	0.11	0.01	13.6	11
	µg/l	G3M		0.12	2.29	15	2.31	2.29	2.28	0.14	6.0	11
	mg/kg	SN4			3.30		3.65	3.30	3.27	0.32	9.8	5
	mg/kg	SO4			3.61		3.84	3.61	3.39	0.59	17.4	3

Participant 5												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	s	s %	n_{stat}
V	µg/l	A1M		0.09	4.25	10	4.27	4.03	4.05	0.14	3.3	11
	µg/l	D2M		0.26	3.11	15	3.17	3.11	3.06	0.15	5.0	11
	µg/l	G3M		0.38	0.88	15	0.91	0.88	0.88	0.06	7.1	9
	mg/kg	SN4			58.4		59.5	58.4	55.0	6.1	11.1	5
	mg/kg	SO4			62.7		68.8	62.7	61.4	6.5	10.6	6
Zn	µg/l	A1M		0.06	33.5	10	33.6	33.0	33.0	1.6	5.0	13
	µg/l	D2M		-0.30	10.2	15	10.0	10.2	10.2	0.4	3.9	12
	µg/l	G3M		-0.47	5.40	15	5.21	5.22	5.35	0.29	5.3	12
	mg/kg	SN4		-0.31	212	15	207	212	214	7	3.3	6
	mg/kg	SO4			203		227	203	208	11	5.5	5

Participant 6												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	s	s %	n_{stat}
Al	µg/l	A1M		-1.19	335	10	315	332	331	22	6.7	16
	µg/l	D2M		-0.64	37.9	15	36.1	37.6	37.9	1.5	4.0	14
	µg/l	G3M		-0.66	14.3	20	13.4	14.2	14.4	1.2	8.6	12
Cd	µg/l	A1M		-0.05	0.75	15	0.75	0.74	0.73	0.05	6.7	12
	µg/l	D2M		-0.16	0.31	15	0.31	0.31	0.31	0.02	6.5	12
	µg/l	G3M		0.33	0.15	15	0.15	0.15	0.15	0.01	6.3	10
Cu	µg/l	A1M		-0.61	12.5	10	12.1	12.1	12.0	1.0	8.2	15
	µg/l	D2M		-0.22	56.8	15	55.9	55.8	56.9	2.9	5.2	14
	µg/l	G3M		0.38	3.57	20	3.70	3.51	3.55	0.27	7.6	12
Fe	µg/l	A1M		-0.23	175	10	173	173	176	8	4.7	15
	µg/l	D2M		-0.32	37.5	15	36.6	37.1	37.7	3.2	8.6	14
	µg/l	G3M		0.56	17.5	20	18.5	17.4	17.6	1.6	8.9	12
Hg	mg/kg	SC4			0.67		0.65	0.67	0.67	0.03	3.8	2
Mn	µg/l	A1M		-0.63	43.5	10	42.1	43.7	43.5	2.0	4.5	15
	µg/l	D2M		-0.14	15.6	15	15.4	15.9	15.8	0.7	4.6	15
	µg/l	G3M		0.36	4.01	15	4.12	4.02	4.02	0.23	5.7	12
Pb	µg/l	A1M		-0.22	4.24	15	4.17	4.20	4.19	0.15	3.6	12
	µg/l	D2M		-0.08	2.18	15	2.17	2.18	2.13	0.12	5.6	12
	µg/l	G3M		-0.33	0.57	15	0.56	0.56	0.56	0.04	7.6	11
Zn	µg/l	A1M		-0.29	33.5	10	33.0	33.0	33.0	1.6	5.0	13
	µg/l	D2M		-0.18	10.2	15	10.1	10.2	10.2	0.4	3.9	12
	µg/l	G3M		-0.56	5.40	15	5.17	5.22	5.35	0.29	5.3	12

Participant 7												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	s	s %	n_{stat}
Al	µg/l	A1M		-0.18	335	10	332	332	331	22	6.7	16
	µg/l	D2M		0.11	37.9	15	38.2	37.6	37.9	1.5	4.0	14
	µg/l	G3M		-0.07	14.3	20	14.2	14.2	14.4	1.2	8.6	12
	g/kg	SO4		0.56	25.9	25	27.7	25.9	25.1	3.3	13.0	6
As	µg/l	A1M		-0.85	1.25	15	1.17	1.21	1.22	0.06	5.3	10
	µg/l	D2M		0.00	0.098	20	0.098	0.098	0.098	0.008	8.4	9
	µg/l	G3M		-0.06	0.18	20	0.18	0.18	0.18	0.01	4.6	7
	mg/kg	SO4		1.23	6.89	25	7.95	6.89	6.82	0.95	14.0	6
Cd	µg/l	A1M		-0.28	0.75	15	0.73	0.74	0.73	0.05	6.7	12
	µg/l	D2M		0.00	0.31	15	0.31	0.31	0.31	0.02	6.5	12
	µg/l	G3M		0.27	0.15	15	0.15	0.15	0.15	0.01	6.3	10
	mg/kg	SO4			0.69		0.76	0.69	0.67	0.11	16.3	6
Co	µg/l	A1M		-0.71	2.25	10	2.17	2.17	2.17	0.07	3.4	11
	µg/l	D2M		0.25	0.32	15	0.33	0.32	0.32	0.02	6.8	9
	µg/l	G3M		-0.30	0.22	15	0.22	0.22	0.22	0.01	3.4	7
	mg/kg	SO4		-0.53	35.7	20	33.8	35.7	35.1	2.6	7.3	6
Cr	µg/l	A1M		-0.12	4.50	15	4.46	4.40	4.40	0.22	5.0	13
	µg/l	D2M		0.08	1.57	15	1.58	1.57	1.56	0.06	3.6	10
	µg/l	G3M		0.10	0.54	15	0.54	0.54	0.55	0.03	5.2	9
	mg/kg	SO4		0.69	58.9	25	64.0	58.9	58.9	6.1	10.3	6
Cu	µg/l	A1M		-0.48	12.5	10	12.2	12.1	12.0	1.0	8.2	15
	µg/l	D2M		0.31	56.8	15	58.1	55.8	56.9	2.9	5.2	14
	µg/l	G3M		1.12	3.57	20	3.97	3.51	3.55	0.27	7.6	12
	mg/kg	SO4		-0.07	70.2	20	69.7	70.2	69.0	3.2	4.6	6
Drw	%	S4M		0.04	98.1	5	98.2	98.1	98.0	0.5	0.5	10
Fe	µg/l	A1M		-0.34	175	10	172	173	176	8	4.7	15
	µg/l	D2M		0.78	37.5	15	39.7	37.1	37.7	3.2	8.6	14
	µg/l	G3M		0.80	17.5	20	18.9	17.4	17.6	1.6	8.9	12
	g/kg	SO4		0.41	34.5	20	35.9	34.5	34.6	2.7	7.7	6
Hg	µg/l	A1Hg		0.00	0.15	20	0.15	0.16	0.15	0.02	9.8	10
	µg/l	D2Hg		-0.55	0.075	25	0.070	0.075	0.074	0.006	8.0	7
	µg/l	G3Hg		-1.54	0.050	25	0.040	0.054	0.053	0.009	16.3	8
	mg/kg	SO4		1.73	0.70	20	0.82	0.70	0.71	0.06	8.7	6
Mn	µg/l	A1M		0.09	43.5	10	43.7	43.7	43.5	2.0	4.5	15
	µg/l	D2M		0.85	15.6	15	16.6	15.9	15.8	0.7	4.6	15
	µg/l	G3M		1.53	4.01	15	4.47	4.02	4.02	0.23	5.7	12
	mg/kg	SO4		0.30	702	15	718	702	705	31	4.3	6
Ni	µg/l	A1M		-0.50	7.25	15	6.98	7.20	7.18	0.34	4.8	12
	µg/l	D2M		2.04	0.54	20	0.65	0.54	0.55	0.01	2.0	7
	µg/l	G3M		0.43	1.56	15	1.61	1.56	1.55	0.08	5.3	9
	mg/kg	SO4		0.49	47.3	20	49.6	47.3	47.7	4.1	8.6	6
Pb	µg/l	A1M		0.16	4.24	15	4.29	4.20	4.19	0.15	3.6	12
	µg/l	D2M		0.00	2.18	15	2.18	2.18	2.13	0.12	5.6	12
	µg/l	G3M		-0.28	0.57	15	0.56	0.56	0.56	0.04	7.6	11
	mg/kg	SO4		0.65	25.8	25	27.9	25.8	26.0	3.0	11.7	6
P_{tot}	g/kg	SO4		0.09	1.11	20	1.12	1.11	1.12	0.10	9.1	6

Participant 7												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	s	s %	n_{stat}
Se	µg/l	A1M		-0.43	1.25	15	1.21	1.21	1.22	0.13	10.7	10
	µg/l	D2M		0.00	0.52	15	0.52	0.52	0.53	0.03	5.3	9
	µg/l	G3M		0.28	1.90	15	1.94	1.90	1.92	0.04	2.3	8
	mg/kg	SO4			2.81		< 3	2.81	3.04	1.88	61.8	4
S_{tot}	g/kg	SO4			4.00		4.62	3.99	4.08	0.38	9.3	4
U	µg/l	A1M		0.18	0.65	15	0.66	0.65	0.63	0.03	5.0	11
	µg/l	D2M		0.51	0.11	25	0.12	0.11	0.11	0.01	13.6	11
	µg/l	G3M		1.16	2.29	15	2.49	2.29	2.28	0.14	6.0	11
V	µg/l	A1M		-0.42	4.25	10	4.16	4.03	4.05	0.14	3.3	11
	µg/l	D2M		0.09	3.11	15	3.13	3.11	3.06	0.15	5.0	11
	µg/l	G3M		-0.06	0.88	15	0.88	0.88	0.88	0.06	7.1	9
	mg/kg	SO4			62.7		61.4	62.7	61.4	6.5	10.6	6
Zn	µg/l	A1M		-0.54	33.5	10	32.6	33.0	33.0	1.6	5.0	13
	µg/l	D2M		0.65	10.2	15	10.7	10.2	10.2	0.4	3.9	12
	µg/l	G3M		1.21	5.40	15	5.89	5.22	5.35	0.29	5.3	12
	mg/kg	SO4			203		211	203	208	11	5.5	5

Participant 8												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	s	s %	n_{stat}
Al	µg/l	A1M		-2.09	335	10	300	332	331	22	6.7	16
	µg/l	D2M		-3.83	37.9	15	27.0	37.6	37.9	1.5	4.0	14
	µg/l	G3M		-4.20	14.3	20	8.3	14.2	14.4	1.2	8.6	12
As	µg/l	A1M		-0.53	1.25	15	1.20	1.21	1.22	0.06	5.3	10
	µg/l	D2M		0.20	0.098	20	0.100	0.098	0.098	0.008	8.4	9
	µg/l	G3M		0.00	0.18	20	0.18	0.18	0.18	0.01	4.6	7
Cd	µg/l	A1M		0.89	0.75	15	0.80	0.74	0.73	0.05	6.7	12
	µg/l	D2M		0.86	0.31	15	0.33	0.31	0.31	0.02	6.5	12
	µg/l	G3M		0.89	0.15	15	0.16	0.15	0.15	0.01	6.3	10
Cr	µg/l	A1M		0.30	4.50	15	4.60	4.40	4.40	0.22	5.0	13
	µg/l	D2M		0.25	1.57	15	1.60	1.57	1.56	0.06	3.6	10
	µg/l	G3M		0.25	0.54	15	0.55	0.54	0.55	0.03	5.2	9
Cu	µg/l	A1M		0.80	12.5	10	13.0	12.1	12.0	1.0	8.2	15
	µg/l	D2M		0.05	56.8	15	57.0	55.8	56.9	2.9	5.2	14
	µg/l	G3M		-1.60	3.57	20	3.00	3.51	3.55	0.27	7.6	12
	mg/kg	SN4		0.07	68.1	20	68.6	68.1	66.4	3.4	5.2	6
Fe	µg/l	A1M		-4.00	175	10	140	173	176	8	4.7	15
	µg/l	D2M		-2.31	37.5	15	31.0	37.1	37.7	3.2	8.6	14
	µg/l	G3M		-3.14	17.5	20	12.0	17.4	17.6	1.6	8.9	12
	g/kg	SN4		2.04	32.9	20	39.6	32.9	33.1	3.7	11.3	6
Hg	µg/l	A1Hg		7.33	0.15	20	0.26	0.16	0.15	0.02	9.8	10
	µg/l	D2Hg		19.73	0.075	25	0.260	0.075	0.074	0.006	8.0	7
	µg/l	G3Hg		17.60	0.050	25	0.160	0.054	0.053	0.009	16.3	8
Mn	µg/l	A1M		-1.15	43.5	10	41.0	43.7	43.5	2.0	4.5	15
	µg/l	D2M		-0.51	15.6	15	15.0	15.9	15.8	0.7	4.6	15
	µg/l	G3M		-1.36	4.01	15	3.60	4.02	4.02	0.23	5.7	12
	mg/kg	SN4		1.46	630	15	699	630	639	37	5.7	6

Participant 8												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	s	s %	n_{stat}
Ni	µg/l	A1M		0.09	7.25	15	7.30	7.20	7.18	0.34	4.8	12
	µg/l	D2M		0.00	0.54	20	0.54	0.54	0.55	0.01	2.0	7
	µg/l	G3M		-0.51	1.56	15	1.50	1.56	1.55	0.08	5.3	9
N_{tot}	g/kg	SN4			4.74		4.76	4.74	4.62	0.26	5.6	5
Pb	µg/l	A1M		0.50	4.24	15	4.40	4.20	4.19	0.15	3.6	12
	µg/l	D2M		0.12	2.18	15	2.20	2.18	2.13	0.12	5.6	12
	µg/l	G3M		-0.23	0.57	15	0.56	0.56	0.56	0.04	7.6	11
P_{tot}	g/kg	SN4		-0.09	1.09	20	1.08	1.09	1.10	0.11	10.1	7
Se	µg/l	A1M		1.60	1.25	15	1.40	1.21	1.22	0.13	10.7	10
	µg/l	D2M		1.03	0.52	15	0.56	0.52	0.53	0.03	5.3	9
	µg/l	G3M		0.00	1.90	15	1.90	1.90	1.92	0.04	2.3	8
	mg/kg	SN4			2.60		1.60	2.60	2.66	0.80	30.0	6
U	µg/l	A1M		0.21	0.65	15	0.66	0.65	0.63	0.03	5.0	11
	µg/l	D2M		0.00	0.11	25	0.11	0.11	0.11	0.01	13.6	11
	µg/l	G3M		-0.52	2.29	15	2.20	2.29	2.28	0.14	6.0	11
Zn	µg/l	A1M		-17.01	33.5	10	5.0	33.0	33.0	1.6	5.0	13
	mg/kg	SN4		0.94	212	15	227	212	214	7	3.3	6

Participant 9												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	s	s %	n_{stat}
N_{tot}	g/kg	SN4			4.74		4.74	4.74	4.62	0.26	5.6	5
P_{tot}	g/kg	SN4		1.05	1.09	20	1.20	1.09	1.10	0.11	10.1	7
TC	g/kg	S4M			87.7		84.1	87.7	87.3	6.1	7.0	5

Participant 10												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	s	s %	n_{stat}
Al	µg/l	A1M		-0.18	335	10	332	332	331	22	6.7	16
	µg/l	D2M		-0.18	37.9	15	37.4	37.6	37.9	1.5	4.0	14
	µg/l	G3M		-0.77	14.3	20	13.2	14.2	14.4	1.2	8.6	12
Cd	µg/l	A1M		0.89	0.75	15	0.80	0.74	0.73	0.05	6.7	12
	µg/l	D2M			0.31	15	*< 0.7*	0.31	0.31	0.02	6.5	12
	µg/l	G3M			0.15	15	*< 0.7*	0.15	0.15	0.01	6.3	10
Co	µg/l	A1M		-0.44	2.25	10	2.20	2.17	2.17	0.07	3.4	11
	µg/l	D2M			0.32	15	*< 0.5*	0.32	0.32	0.02	6.8	9
	µg/l	G3M			0.22	15	*< 0.5*	0.22	0.22	0.01	3.4	7
Cr	µg/l	A1M		-0.30	4.50	15	4.40	4.40	4.40	0.22	5.0	13
	µg/l	D2M		-0.59	1.57	15	1.50	1.57	1.56	0.06	3.6	10
	µg/l	G3M			0.54	15	*< 1*	0.54	0.55	0.03	5.2	9
Cu	µg/l	A1M		-0.64	12.5	10	12.1	12.1	12.0	1.0	8.2	15
	µg/l	D2M		-0.33	56.8	15	55.4	55.8	56.9	2.9	5.2	14
	µg/l	G3M		-0.20	3.57	20	3.50	3.51	3.55	0.27	7.6	12
Fe	µg/l	A1M		-0.70	175	10	169	173	176	8	4.7	15
	µg/l	D2M		-1.14	37.5	15	34.3	37.1	37.7	3.2	8.6	14
	µg/l	G3M		-1.43	17.5	20	15.0	17.4	17.6	1.6	8.9	12
Mn	µg/l	A1M		-0.69	43.5	10	42.0	43.7	43.5	2.0	4.5	15
	µg/l	D2M		-0.68	15.6	15	14.8	15.9	15.8	0.7	4.6	15
	µg/l	G3M		-1.03	4.01	15	3.70	4.02	4.02	0.23	5.7	12

Participant 10												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	s	s %	n_{stat}
Ni	µg/l	A1M		0.28	7.25	15	7.40	7.20	7.18	0.34	4.8	12
	µg/l	D2M			0.54	20	*< 2*	0.54	0.55	0.01	2.0	7
	µg/l	G3M		10.60	1.56	15	2.80	1.56	1.55	0.08	5.3	9
Pb	µg/l	A1M		2.70	4.24	15	5.10	4.20	4.19	0.15	3.6	12
	µg/l	D2M			2.18	15	*< 5*	2.18	2.13	0.12	5.6	12
	µg/l	G3M			0.57	15	*< 5*	0.56	0.56	0.04	7.6	11
Ti	µg/l	A1M		-0.80	22.5	10	21.6	21.6	21.7	0.9	4.0	9
	µg/l	D2M		-0.66	5.26	15	5.00	5.26	5.30	0.29	5.4	7
	µg/l	G3M		-1.08	16.0	15	14.7	16.0	16.1	0.9	5.9	8
V	µg/l	A1M		-1.18	4.25	10	4.00	4.03	4.05	0.14	3.3	11
	µg/l	D2M		-0.47	3.11	15	3.00	3.11	3.06	0.15	5.0	11
	µg/l	G3M			0.88	15	*< 1*	0.88	0.88	0.06	7.1	9
Zn	µg/l	A1M		0.30	33.5	10	34.0	33.0	33.0	1.6	5.0	13
	µg/l	D2M		0.26	10.2	15	10.4	10.2	10.2	0.4	3.9	12
	µg/l	G3M		-0.49	5.40	15	5.20	5.22	5.35	0.29	5.3	12

Participant 11												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	s	s %	n_{stat}
Al	µg/l	A1M		-0.12	335	10	333	332	331	22	6.7	16
	µg/l	D2M		1.06	37.9	15	40.9	37.6	37.9	1.5	4.0	14
	µg/l	G3M		1.05	14.3	20	15.8	14.2	14.4	1.2	8.6	12
	g/kg	SN4			22.4		21.8	22.4	20.8	4.1	19.9	4
As	µg/l	A1M		0.32	1.25	15	1.28	1.21	1.22	0.06	5.3	10
	µg/l	D2M		-0.31	0.098	20	0.095	0.098	0.098	0.008	8.4	9
	µg/l	G3M		-0.17	0.18	20	0.18	0.18	0.18	0.01	4.6	7
	mg/kg	SN4			6.65		6.67	6.65	6.36	0.66	10.4	5
Cd	µg/l	A1M		-1.16	0.75	15	0.69	0.74	0.73	0.05	6.7	12
	µg/l	D2M		-0.52	0.31	15	0.30	0.31	0.31	0.02	6.5	12
	µg/l	G3M		-0.18	0.15	15	0.15	0.15	0.15	0.01	6.3	10
	mg/kg	SN4			0.73		0.67	0.73	0.77	0.13	16.3	5
Co	µg/l	A1M		0.09	2.25	10	2.26	2.17	2.17	0.07	3.4	11
	µg/l	D2M		0.92	0.32	15	0.34	0.32	0.32	0.02	6.8	9
	µg/l	G3M		0.12	0.22	15	0.22	0.22	0.22	0.01	3.4	7
	mg/kg	SN4			34.0		35.7	34.0	34.0	2.1	6.2	5
Cr	µg/l	A1M		1.16	4.50	15	4.89	4.40	4.40	0.22	5.0	13
	µg/l	D2M		0.76	1.57	15	1.66	1.57	1.56	0.06	3.6	10
	µg/l	G3M		1.56	0.54	15	0.60	0.54	0.55	0.03	5.2	9
	mg/kg	SN4		0.36	56.3	25	58.8	56.3	55.3	4.9	8.9	6
Cu	µg/l	A1M		0.80	12.5	10	13.0	12.1	12.0	1.0	8.2	15
	µg/l	D2M		0.99	56.8	15	61.0	55.8	56.9	2.9	5.2	14
	µg/l	G3M		1.15	3.57	20	3.98	3.51	3.55	0.27	7.6	12
	mg/kg	SN4		0.03	68.1	20	68.3	68.1	66.4	3.4	5.2	6
Drw	%	S4M		-0.04	98.1	5	98.0	98.1	98.0	0.5	0.5	10
Fe	µg/l	A1M		0.46	175	10	179	173	176	8	4.7	15
	µg/l	D2M		0.18	37.5	15	38.0	37.1	37.7	3.2	8.6	14
	µg/l	G3M		0.00	17.5	20	17.5	17.4	17.6	1.6	8.9	12
	g/kg	SN4		0.15	32.9	20	33.4	32.9	33.1	3.7	11.3	6

Participant 11												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	s	s %	n_{stat}
Hg	µg/l	A1Hg		0.60	0.15	20	0.16	0.16	0.15	0.02	9.8	10
	µg/l	D2Hg		-0.14	0.075	25	0.074	0.075	0.074	0.006	8.0	7
	µg/l	G3Hg		0.96	0.050	25	0.056	0.054	0.053	0.009	16.3	8
	mg/kg	SN4			0.73		0.73	0.73	0.73	0.03	4.1	5
Mn	µg/l	A1M		0.92	43.5	10	45.5	43.7	43.5	2.0	4.5	15
	µg/l	D2M		1.11	15.6	15	16.9	15.9	15.8	0.7	4.6	15
	µg/l	G3M		0.80	4.01	15	4.25	4.02	4.02	0.23	5.7	12
	mg/kg	SN4		0.70	630	15	663	630	639	37	5.7	6
Ni	µg/l	A1M		0.59	7.25	15	7.57	7.20	7.18	0.34	4.8	12
	µg/l	D2M		0.02	0.54	20	0.54	0.54	0.55	0.01	2.0	7
	µg/l	G3M		1.03	1.56	15	1.68	1.56	1.55	0.08	5.3	9
	mg/kg	SN4			48.6		50.2	48.6	47.3	2.7	5.6	5
Pb	µg/l	A1M		-0.16	4.24	15	4.19	4.20	4.19	0.15	3.6	12
	µg/l	D2M		0.12	2.18	15	2.20	2.18	2.13	0.12	5.6	12
	µg/l	G3M		0.02	0.57	15	0.57	0.56	0.56	0.04	7.6	11
	mg/kg	SN4			28.7		27.6	28.7	28.5	1.9	6.7	5
P_{tot}	g/kg	SN4		-0.05	1.09	20	1.09	1.09	1.10	0.11	10.1	7
Se	µg/l	A1M		1.28	1.25	15	1.37	1.21	1.22	0.13	10.7	10
	µg/l	D2M		-0.31	0.52	15	0.51	0.52	0.53	0.03	5.3	9
	µg/l	G3M		0.56	1.90	15	1.98	1.90	1.92	0.04	2.3	8
	mg/kg	SN4			2.60		3.72	2.60	2.66	0.80	30.0	6
S_{tot}	g/kg	SN4			4.37		4.68	4.37	4.25	0.47	11.1	4
Ti	µg/l	A1M		-0.89	22.5	10	21.5	21.6	21.7	0.9	4.0	9
	µg/l	D2M		0.28	5.26	15	5.37	5.26	5.30	0.29	5.4	7
	µg/l	G3M		0.08	16.0	15	16.1	16.0	16.1	0.9	5.9	8
	mg/kg	SN4			1800		1842	1800	1681	244	14.5	3
U	µg/l	A1M		119.18	0.65	15	6.46	0.65	0.63	0.03	5.0	11
	µg/l	D2M		-0.73	0.11	25	0.10	0.11	0.11	0.01	13.6	11
	µg/l	G3M		-0.76	2.29	15	2.16	2.29	2.28	0.14	6.0	11
	mg/kg	SN4			3.30		3.30	3.30	3.27	0.32	9.8	5
V	µg/l	A1M		-1.04	4.25	10	4.03	4.03	4.05	0.14	3.3	11
	µg/l	D2M		0.17	3.11	15	3.15	3.11	3.06	0.15	5.0	11
	µg/l	G3M		-0.71	0.88	15	0.83	0.88	0.88	0.06	7.1	9
	mg/kg	SN4			58.4		58.7	58.4	55.0	6.1	11.1	5
Zn	µg/l	A1M		-0.60	33.5	10	32.5	33.0	33.0	1.6	5.0	13
	µg/l	D2M		0.65	10.2	15	10.7	10.2	10.2	0.4	3.9	12
	µg/l	G3M		0.44	5.40	15	5.58	5.22	5.35	0.29	5.3	12
	mg/kg	SN4		-0.06	212	15	211	212	214	7	3.3	6

Participant 12												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	s	s %	n_{stat}
Al	µg/l	A1M		-2.33	335	10	296	332	331	22	6.7	16
As	µg/l	A1M			1.25	15	*< 9.5*	1.21	1.22	0.06	5.3	10
Cd	µg/l	A1M		-3.91	0.75	15	0.53	0.74	0.73	0.05	6.7	12
Co	µg/l	A1M			2.25	10	*< 2.0*	2.17	2.17	0.07	3.4	11
Cr	µg/l	A1M		-0.30	4.50	15	4.40	4.40	4.40	0.22	5.0	13
Cu	µg/l	A1M		-3.68	12.5	10	10.2	12.1	12.0	1.0	8.2	15
Drw	%	S4M		0.01	98.1	5	98.1	98.1	98.0	0.5	0.5	10

Participant 12												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	s	s %	n_{stat}
Fe	µg/l	A1M		-1.26	175	10	164	173	176	8	4.7	15
Hg	µg/l	A1Hg		-1.47	0.15	20	0.13	0.16	0.15	0.02	9.8	10
	mg/kg	SO4		0.03	0.70	20	0.70	0.70	0.71	0.06	8.7	6
Mn	µg/l	A1M		-0.92	43.5	10	41.5	43.7	43.5	2.0	4.5	15
Ni	µg/l	A1M		-1.93	7.25	15	6.20	7.20	7.18	0.34	4.8	12
Pb	µg/l	A1M			4.24	15	*< 5.6*	4.20	4.19	0.15	3.6	12
Zn	µg/l	A1M		-2.63	33.5	10	29.1	33.0	33.0	1.6	5.0	13

Participant 13												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	s	s %	n_{stat}
Al	µg/l	A1M		-0.60	335	10	325	332	331	22	6.7	16
	µg/l	D2M		-0.42	37.9	15	36.7	37.6	37.9	1.5	4.0	14
	µg/l	G3M		-0.42	14.3	20	13.7	14.2	14.4	1.2	8.6	12
As	µg/l	A1M		-0.32	1.25	15	1.22	1.21	1.22	0.06	5.3	10
	µg/l	D2M		-1.70	0.098	20	0.081	0.098	0.098	0.008	8.4	9
	µg/l	G3M		0.44	0.18	20	0.19	0.18	0.18	0.01	4.6	7
	mg/kg	SN4			6.65		7.04	6.65	6.36	0.66	10.4	5
Cd	µg/l	A1M		-0.87	0.75	15	0.70	0.74	0.73	0.05	6.7	12
	µg/l	D2M		0.13	0.31	15	0.31	0.31	0.31	0.02	6.5	12
	µg/l	G3M		0.36	0.15	15	0.15	0.15	0.15	0.01	6.3	10
	mg/kg	SN4			0.73		0.73	0.73	0.77	0.13	16.3	5
Co	µg/l	A1M		-0.18	2.25	10	2.23	2.17	2.17	0.07	3.4	11
	µg/l	D2M		-0.54	0.32	15	0.31	0.32	0.32	0.02	6.8	9
	µg/l	G3M		-0.18	0.22	15	0.22	0.22	0.22	0.01	3.4	7
	mg/kg	SN4			34.0		35.8	34.0	34.0	2.1	6.2	5
Cr	µg/l	A1M		-0.12	4.50	15	4.46	4.40	4.40	0.22	5.0	13
	µg/l	D2M		-0.08	1.57	15	1.56	1.57	1.56	0.06	3.6	10
	µg/l	G3M		0.42	0.54	15	0.56	0.54	0.55	0.03	5.2	9
	mg/kg	SN4		-0.49	56.3	25	52.9	56.3	55.3	4.9	8.9	6
Cu	µg/l	A1M		-0.64	12.5	10	12.1	12.1	12.0	1.0	8.2	15
	µg/l	D2M		-0.42	56.8	15	55.0	55.8	56.9	2.9	5.2	14
	µg/l	G3M		-0.14	3.57	20	3.52	3.51	3.55	0.27	7.6	12
	mg/kg	SN4		0.10	68.1	20	68.8	68.1	66.4	3.4	5.2	6
Drw	%	S4M		0.41	98.1	5	99.1	98.1	98.0	0.5	0.5	10
Fe	µg/l	A1M		-0.69	175	10	169	173	176	8	4.7	15
	µg/l	D2M		-0.11	37.5	15	37.2	37.1	37.7	3.2	8.6	14
	µg/l	G3M		0.51	17.5	20	18.4	17.4	17.6	1.6	8.9	12
	g/kg	SN4		-0.06	32.9	20	32.7	32.9	33.1	3.7	11.3	6
Hg	µg/l	A1Hg		0.60	0.15	20	0.16	0.16	0.15	0.02	9.8	10
	µg/l	D2Hg		-0.02	0.075	25	0.075	0.075	0.074	0.006	8.0	7
	µg/l	G3Hg		0.05	0.050	25	0.050	0.054	0.053	0.009	16.3	8
	mg/kg	SN4			0.73		0.69	0.73	0.73	0.03	4.1	5
Mn	µg/l	A1M		0.14	43.5	10	43.8	43.7	43.5	2.0	4.5	15
	µg/l	D2M		0.17	15.6	15	15.8	15.9	15.8	0.7	4.6	15
	µg/l	G3M		-0.10	4.01	15	3.98	4.02	4.02	0.23	5.7	12
	mg/kg	SN4		-0.11	630	15	625	630	639	37	5.7	6

Participant 13												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	s	s %	n_{stat}
Ni	µg/l	A1M		-0.28	7.25	15	7.10	7.20	7.18	0.34	4.8	12
	µg/l	D2M		0.22	0.54	20	0.55	0.54	0.55	0.01	2.0	7
	µg/l	G3M		0.17	1.56	15	1.58	1.56	1.55	0.08	5.3	9
	mg/kg	SN4			48.6		48.6	48.6	47.3	2.7	5.6	5
N_{tot}	g/kg	SN4			4.74		4.26	4.74	4.62	0.26	5.6	5
Pb	µg/l	A1M		-0.31	4.24	15	4.14	4.20	4.19	0.15	3.6	12
	µg/l	D2M		0.43	2.18	15	2.25	2.18	2.13	0.12	5.6	12
	µg/l	G3M		1.92	0.57	15	0.65	0.56	0.56	0.04	7.6	11
	mg/kg	SN4			28.7		29.0	28.7	28.5	1.9	6.7	5
P_{tot}	g/kg	SN4		0.46	1.09	20	1.14	1.09	1.10	0.11	10.1	7
Se	µg/l	A1M		-0.43	1.25	15	1.21	1.21	1.22	0.13	10.7	10
	µg/l	D2M		1.49	0.52	15	0.58	0.52	0.53	0.03	5.3	9
	µg/l	G3M		-0.07	1.90	15	1.89	1.90	1.92	0.04	2.3	8
	mg/kg	SN4			2.60		2.64	2.60	2.66	0.80	30.0	6
S_{tot}	g/kg	SN4			4.37		4.46	4.37	4.25	0.47	11.1	4
U	µg/l	A1M		-0.25	0.65	15	0.64	0.65	0.63	0.03	5.0	11
	µg/l	D2M		1.60	0.11	25	0.13	0.11	0.11	0.01	13.6	11
	µg/l	G3M		0.00	2.29	15	2.29	2.29	2.28	0.14	6.0	11
V	µg/l	A1M		-0.52	4.25	10	4.14	4.03	4.05	0.14	3.3	11
	µg/l	D2M		0.00	3.11	15	3.11	3.11	3.06	0.15	5.0	11
	µg/l	G3M		0.26	0.88	15	0.90	0.88	0.88	0.06	7.1	9
	mg/kg	SN4			58.4		53.3	58.4	55.0	6.1	11.1	5
Zn	µg/l	A1M		-0.42	33.5	10	32.8	33.0	33.0	1.6	5.0	13
	µg/l	D2M		-0.71	10.2	15	9.7	10.2	10.2	0.4	3.9	12
	µg/l	G3M		-0.62	5.40	15	5.15	5.22	5.35	0.29	5.3	12
	mg/kg	SN4		-0.18	212	15	209	212	214	7	3.3	6

Participant 14												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	s	s %	n_{stat}
Al	µg/l	A1M		-0.24	335	10	331	332	331	22	6.7	16
	µg/l	D2M		-0.32	37.9	15	37.0	37.6	37.9	1.5	4.0	14
	µg/l	G3M		1.12	14.3	20	15.9	14.2	14.4	1.2	8.6	12
	g/kg	SN4			22.4		23.7	22.4	20.8	4.1	19.9	4
As	µg/l	A1M		-0.75	1.25	15	1.18	1.21	1.22	0.06	5.3	10
	µg/l	D2M		-0.51	0.098	20	0.093	0.098	0.098	0.008	8.4	9
	µg/l	G3M		-0.83	0.18	20	0.17	0.18	0.18	0.01	4.6	7
	mg/kg	SN4			6.65		6.12	6.65	6.36	0.66	10.4	5
Cd	µg/l	A1M		-0.80	0.75	15	0.71	0.74	0.73	0.05	6.7	12
	µg/l	D2M		-0.47	0.31	15	0.30	0.31	0.31	0.02	6.5	12
	µg/l	G3M		0.09	0.15	15	0.15	0.15	0.15	0.01	6.3	10
	mg/kg	SN4			0.73		0.69	0.73	0.77	0.13	16.3	5
Co	µg/l	A1M		-0.89	2.25	10	2.15	2.17	2.17	0.07	3.4	11
	µg/l	D2M		0.25	0.32	15	0.33	0.32	0.32	0.02	6.8	9
	µg/l	G3M		-0.12	0.22	15	0.22	0.22	0.22	0.01	3.4	7
	mg/kg	SN4			34.0		30.6	34.0	34.0	2.1	6.2	5

Participant 14												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	s	s %	n_{stat}
Cr	µg/l	A1M		-0.71	4.50	15	4.26	4.40	4.40	0.22	5.0	13
	µg/l	D2M		-0.51	1.57	15	1.51	1.57	1.56	0.06	3.6	10
	µg/l	G3M		-0.37	0.54	15	0.53	0.54	0.55	0.03	5.2	9
	mg/kg	SN4		-0.33	56.3	25	54.0	56.3	55.3	4.9	8.9	6
Cu	µg/l	A1M		-1.44	12.5	10	11.6	12.1	12.0	1.0	8.2	15
	µg/l	D2M		-0.54	56.8	15	54.5	55.8	56.9	2.9	5.2	14
	µg/l	G3M		-0.36	3.57	20	3.44	3.51	3.55	0.27	7.6	12
	mg/kg	SN4		-1.17	68.1	20	60.1	68.1	66.4	3.4	5.2	6
Drw	%	S4M		0.00	98.1	5	98.1	98.1	98.0	0.5	0.5	10
Fe	µg/l	A1M		-0.11	175	10	174	173	176	8	4.7	15
	µg/l	D2M		-0.21	37.5	15	36.9	37.1	37.7	3.2	8.6	14
	µg/l	G3M		-0.11	17.5	20	17.3	17.4	17.6	1.6	8.9	12
	g/kg	SN4		0.06	32.9	20	33.1	32.9	33.1	3.7	11.3	6
Hg	µg/l	A1Hg		0.87	0.15	20	0.16	0.16	0.15	0.02	9.8	10
	µg/l	D2Hg		0.67	0.075	25	0.081	0.075	0.074	0.006	8.0	7
	µg/l	G3Hg		0.99	0.050	25	0.056	0.054	0.053	0.009	16.3	8
	mg/kg	SC4			0.67		0.69	0.67	0.67	0.03	3.8	2
Mn	µg/l	A1M		0.92	43.5	10	45.5	43.7	43.5	2.0	4.5	15
	µg/l	D2M		0.34	15.6	15	16.0	15.9	15.8	0.7	4.6	15
	µg/l	G3M		0.33	4.01	15	4.11	4.02	4.02	0.23	5.7	12
	mg/kg	SN4		-0.23	630	15	619	630	639	37	5.7	6
Ni	µg/l	A1M		-0.46	7.25	15	7.00	7.20	7.18	0.34	4.8	12
	µg/l	D2M		0.41	0.54	20	0.56	0.54	0.55	0.01	2.0	7
	µg/l	G3M		-0.68	1.56	15	1.48	1.56	1.55	0.08	5.3	9
	mg/kg	SN4			48.6		44.2	48.6	47.3	2.7	5.6	5
N_{tot}	g/kg	SN4			4.74		2.41	4.74	4.62	0.26	5.6	5
Pb	µg/l	A1M		-0.94	4.24	15	3.94	4.20	4.19	0.15	3.6	12
	µg/l	D2M		-1.28	2.18	15	1.97	2.18	2.13	0.12	5.6	12
	µg/l	G3M		-1.29	0.57	15	0.52	0.56	0.56	0.04	7.6	11
	mg/kg	SN4			28.7		26.1	28.7	28.5	1.9	6.7	5
P_{tot}	g/kg	SN4		1.65	1.09	20	1.27	1.09	1.10	0.11	10.1	7
Se	µg/l	A1M		-0.21	1.25	15	1.23	1.21	1.22	0.13	10.7	10
	µg/l	D2M		-0.38	0.52	15	0.51	0.52	0.53	0.03	5.3	9
	µg/l	G3M		-1.33	1.90	15	1.71	1.90	1.92	0.04	2.3	8
	mg/kg	SN4			2.60		2.05	2.60	2.66	0.80	30.0	6
S_{tot}	g/kg	SN4			4.37		4.27	4.37	4.25	0.47	11.1	4
TC	g/kg	S4M			87.7		87.7	87.7	87.3	6.1	7.0	5
Ti	µg/l	A1M		-1.07	22.5	10	21.3	21.6	21.7	0.9	4.0	9
	µg/l	D2M		-0.46	5.26	15	5.08	5.26	5.30	0.29	5.4	7
	µg/l	G3M		-0.42	16.0	15	15.5	16.0	16.1	0.9	5.9	8
	mg/kg	SN4			1800		1800	1800	1681	244	14.5	3
U	µg/l	A1M		-0.86	0.65	15	0.61	0.65	0.63	0.03	5.0	11
	µg/l	D2M		-0.58	0.11	25	0.10	0.11	0.11	0.01	13.6	11
	µg/l	G3M		-0.99	2.29	15	2.12	2.29	2.28	0.14	6.0	11
	mg/kg	SN4			3.30		3.25	3.30	3.27	0.32	9.8	5

Participant 14												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	s	s %	n_{stat}
V	µg/l	A1M		-1.04	4.25	10	4.03	4.03	4.05	0.14	3.3	11
	µg/l	D2M		-0.43	3.11	15	3.01	3.11	3.06	0.15	5.0	11
	µg/l	G3M		-0.52	0.88	15	0.85	0.88	0.88	0.06	7.1	9
	mg/kg	SN4			58.4		58.4	58.4	55.0	6.1	11.1	5
Zn	µg/l	A1M		-1.25	33.5	10	31.4	33.0	33.0	1.6	5.0	13
	µg/l	D2M		-0.92	10.2	15	9.5	10.2	10.2	0.4	3.9	12
	µg/l	G3M		-0.99	5.40	15	5.00	5.22	5.35	0.29	5.3	12
	mg/kg	SN4		0.25	212	15	216	212	214	7	3.3	6

Participant 15												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	s	s %	n_{stat}
Al	µg/l	A1M		-1.01	335	10	318	332	331	22	6.7	16
	µg/l	D2M		-0.04	37.9	15	37.8	37.6	37.9	1.5	4.0	14
	µg/l	G3M		0.00	14.3	20	14.3	14.2	14.4	1.2	8.6	12
	g/kg	SN4			22.4		14.7	22.4	20.8	4.1	19.9	4
As	µg/l	A1M		-1.07	1.25	15	1.15	1.21	1.22	0.06	5.3	10
	µg/l	D2M		-0.20	0.098	20	0.096	0.098	0.098	0.008	8.4	9
	µg/l	G3M		0.00	0.18	20	0.18	0.18	0.18	0.01	4.6	7
	mg/kg	SN4			6.65		5.34	6.65	6.36	0.66	10.4	5
Cd	µg/l	A1M		0.37	0.75	15	0.77	0.74	0.73	0.05	6.7	12
	µg/l	D2M		0.52	0.31	15	0.32	0.31	0.31	0.02	6.5	12
	µg/l	G3M		1.16	0.15	15	0.16	0.15	0.15	0.01	6.3	10
	mg/kg	SN4			0.73		0.98	0.73	0.77	0.13	16.3	5
Co	µg/l	A1M		-0.44	2.25	10	2.20	2.17	2.17	0.07	3.4	11
	µg/l	D2M		1.63	0.32	15	0.36	0.32	0.32	0.02	6.8	9
	µg/l	G3M		-0.18	0.22	15	0.22	0.22	0.22	0.01	3.4	7
	mg/kg	SN4			34.0		33.7	34.0	34.0	2.1	6.2	5
Cr	µg/l	A1M		-0.18	4.50	15	4.44	4.40	4.40	0.22	5.0	13
	µg/l	D2M		4.25	1.57	15	2.07	1.57	1.56	0.06	3.6	10
	µg/l	G3M		0.64	0.54	15	0.57	0.54	0.55	0.03	5.2	9
	mg/kg	SN4		-1.28	56.3	25	47.3	56.3	55.3	4.9	8.9	6
Cu	µg/l	A1M		0.48	12.5	10	12.8	12.1	12.0	1.0	8.2	15
	µg/l	D2M		0.68	56.8	15	59.7	55.8	56.9	2.9	5.2	14
	µg/l	G3M		0.11	3.57	20	3.61	3.51	3.55	0.27	7.6	12
	mg/kg	SN4		-0.03	68.1	20	67.9	68.1	66.4	3.4	5.2	6
Drw	%	S4M		0.00	98.1	5	98.1	98.1	98.0	0.5	0.5	10
Fe	µg/l	A1M		-0.23	175	10	173	173	176	8	4.7	15
	µg/l	D2M		1.99	37.5	15	43.1	37.1	37.7	3.2	8.6	14
	µg/l	G3M		1.89	17.5	20	20.8	17.4	17.6	1.6	8.9	12
	g/kg	SN4		-1.46	32.9	20	28.1	32.9	33.1	3.7	11.3	6
Hg	µg/l	A1Hg		0.53	0.15	20	0.16	0.16	0.15	0.02	9.8	10
	µg/l	D2Hg		0.22	0.075	25	0.077	0.075	0.074	0.006	8.0	7
	µg/l	G3Hg		0.75	0.050	25	0.055	0.054	0.053	0.009	16.3	8
	mg/kg	SN4			0.73		0.72	0.73	0.73	0.03	4.1	5
Mn	µg/l	A1M		-0.64	43.5	10	42.1	43.7	43.5	2.0	4.5	15
	µg/l	D2M		0.26	15.6	15	15.9	15.9	15.8	0.7	4.6	15
	µg/l	G3M		0.13	4.01	15	4.05	4.02	4.02	0.23	5.7	12
	mg/kg	SN4		-0.74	630	15	595	630	639	37	5.7	6

Participant 15												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	s	s %	n_{stat}
Ni	µg/l	A1M		-0.48	7.25	15	6.99	7.20	7.18	0.34	4.8	12
	µg/l	D2M		269.63	0.54	20	15.10	0.54	0.55	0.01	2.0	7
	µg/l	G3M		0.34	1.56	15	1.60	1.56	1.55	0.08	5.3	9
	mg/kg	SN4			48.6		44.8	48.6	47.3	2.7	5.6	5
N_{tot}	g/kg	SN4			4.74		4.46	4.74	4.62	0.26	5.6	5
Pb	µg/l	A1M		0.13	4.24	15	4.28	4.20	4.19	0.15	3.6	12
	µg/l	D2M		0.61	2.18	15	2.28	2.18	2.13	0.12	5.6	12
	µg/l	G3M		0.21	0.57	15	0.58	0.56	0.56	0.04	7.6	11
	mg/kg	SN4			28.7		31.3	28.7	28.5	1.9	6.7	5
P_{tot}	g/kg	SN4		-1.34	1.09	20	0.94	1.09	1.10	0.11	10.1	7
Se	µg/l	A1M		-0.64	1.25	15	1.19	1.21	1.22	0.13	10.7	10
	µg/l	D2M		-0.64	0.52	15	0.50	0.52	0.53	0.03	5.3	9
	µg/l	G3M		-0.35	1.90	15	1.85	1.90	1.92	0.04	2.3	8
	mg/kg	SN4			2.60		3.40	2.60	2.66	0.80	30.0	6
Ti	µg/l	A1M		-0.44	22.5	10	22.0	21.6	21.7	0.9	4.0	9
	µg/l	D2M		1.55	5.26	15	5.87	5.26	5.30	0.29	5.4	7
	µg/l	G3M		0.42	16.0	15	16.5	16.0	16.1	0.9	5.9	8
U	µg/l	A1M		0.06	0.65	15	0.65	0.65	0.63	0.03	5.0	11
	µg/l	D2M		0.80	0.11	25	0.12	0.11	0.11	0.01	13.6	11
	µg/l	G3M		0.82	2.29	15	2.43	2.29	2.28	0.14	6.0	11
	mg/kg	SN4			3.30		3.40	3.30	3.27	0.32	9.8	5
V	µg/l	A1M		-0.80	4.25	10	4.08	4.03	4.05	0.14	3.3	11
	µg/l	D2M		0.21	3.11	15	3.16	3.11	3.06	0.15	5.0	11
	µg/l	G3M		0.70	0.88	15	0.93	0.88	0.88	0.06	7.1	9
	mg/kg	SN4			58.4		45.0	58.4	55.0	6.1	11.1	5
Zn	µg/l	A1M		-0.18	33.5	10	33.2	33.0	33.0	1.6	5.0	13
	µg/l	D2M		0.39	10.2	15	10.5	10.2	10.2	0.4	3.9	12
	µg/l	G3M		3.75	5.40	15	6.92	5.22	5.35	0.29	5.3	12
	mg/kg	SN4		0.06	212	15	213	212	214	7	3.3	6

Participant 16												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	s	s %	n_{stat}
Al	µg/l	A1M		2.30	335	10	373	332	331	22	6.7	16
	µg/l	D2M		0.00	37.9	15	37.9	37.6	37.9	1.5	4.0	14
	µg/l	G3M		-0.56	14.3	20	13.5	14.2	14.4	1.2	8.6	12
	g/kg	SO4		-0.62	25.9	25	23.9	25.9	25.1	3.3	13.0	6
As	µg/l	A1M		1.10	1.25	15	1.35	1.21	1.22	0.06	5.3	10
	µg/l	D2M		1.33	0.098	20	0.111	0.098	0.098	0.008	8.4	9
	µg/l	G3M		3.17	0.18	20	0.24	0.18	0.18	0.01	4.6	7
	mg/kg	SO4		-1.75	6.89	25	5.39	6.89	6.82	0.95	14.0	6
Cd	µg/l	A1M		-2.10	0.75	15	0.63	0.74	0.73	0.05	6.7	12
	µg/l	D2M		-2.15	0.31	15	0.26	0.31	0.31	0.02	6.5	12
	µg/l	G3M		-1.87	0.15	15	0.13	0.15	0.15	0.01	6.3	10
	mg/kg	SO4			0.69		0.58	0.69	0.67	0.11	16.3	6
Co	µg/l	A1M		-1.66	2.25	10	2.06	2.17	2.17	0.07	3.4	11
	µg/l	D2M		-1.42	0.32	15	0.29	0.32	0.32	0.02	6.8	9
	µg/l	G3M		-2.48	0.22	15	0.18	0.22	0.22	0.01	3.4	7
	mg/kg	SO4		0.07	35.7	20	36.0	35.7	35.1	2.6	7.3	6

Participant 16												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	s	s %	n_{stat}
Cr	µg/l	A1M		-1.16	4.50	15	4.11	4.40	4.40	0.22	5.0	13
	µg/l	D2M		-0.65	1.57	15	1.49	1.57	1.56	0.06	3.6	10
	µg/l	G3M		-0.84	0.54	15	0.51	0.54	0.55	0.03	5.2	9
	mg/kg	SO4		0.00	58.9	25	58.9	58.9	58.9	6.1	10.3	6
Cu	µg/l	A1M		-1.78	12.5	10	11.4	12.1	12.0	1.0	8.2	15
	µg/l	D2M		0.75	56.8	15	60.0	55.8	56.9	2.9	5.2	14
	µg/l	G3M		-0.65	3.57	20	3.34	3.51	3.55	0.27	7.6	12
	mg/kg	SO4		-1.00	70.2	20	63.2	70.2	69.0	3.2	4.6	6
Fe	µg/l	A1M		1.31	175	10	186	173	176	8	4.7	15
	µg/l	D2M		0.85	37.5	15	39.9	37.1	37.7	3.2	8.6	14
	µg/l	G3M		0.75	17.5	20	18.8	17.4	17.6	1.6	8.9	12
	g/kg	SO4		-0.41	34.5	20	33.1	34.5	34.6	2.7	7.7	6
Hg	µg/l	A1Hg		-1.67	0.15	20	0.13	0.16	0.15	0.02	9.8	10
	µg/l	D2Hg		-1.28	0.075	25	0.063	0.075	0.074	0.006	8.0	7
	µg/l	G3Hg		-0.64	0.050	25	0.046	0.054	0.053	0.009	16.3	8
	mg/kg	SO4		-0.13	0.70	20	0.69	0.70	0.71	0.06	8.7	6
Mn	µg/l	A1M		1.49	43.5	10	46.7	43.7	43.5	2.0	4.5	15
	µg/l	D2M		0.97	15.6	15	16.7	15.9	15.8	0.7	4.6	15
	µg/l	G3M		0.07	4.01	15	4.03	4.02	4.02	0.23	5.7	12
	mg/kg	SO4		-0.29	702	15	687	702	705	31	4.3	6
Ni	µg/l	A1M		-1.08	7.25	15	6.66	7.20	7.18	0.34	4.8	12
	µg/l	D2M		0.07	0.54	20	0.54	0.54	0.55	0.01	2.0	7
	µg/l	G3M		-1.25	1.56	15	1.41	1.56	1.55	0.08	5.3	9
	mg/kg	SO4		0.06	47.3	20	47.6	47.3	47.7	4.1	8.6	6
Pb	µg/l	A1M		-1.14	4.24	15	3.88	4.20	4.19	0.15	3.6	12
	µg/l	D2M		-1.67	2.18	15	1.91	2.18	2.13	0.12	5.6	12
	µg/l	G3M		-2.06	0.57	15	0.48	0.56	0.56	0.04	7.6	11
	mg/kg	SO4		0.30	25.8	25	26.8	25.8	26.0	3.0	11.7	6
P_{tot}	g/kg	SO4		-0.86	1.11	20	1.01	1.11	1.12	0.10	9.1	6
Se	µg/l	A1M		-3.43	1.25	15	0.93	1.21	1.22	0.13	10.7	10
	µg/l	D2M		-0.23	0.52	15	0.51	0.52	0.53	0.03	5.3	9
	µg/l	G3M		-2.26	1.90	15	1.58	1.90	1.92	0.04	2.3	8
	mg/kg	SO4			2.81		5.53	2.81	3.04	1.88	61.8	4
S_{tot}	g/kg	SO4			4.00		3.94	3.99	4.08	0.38	9.3	4
Ti	µg/l	A1M		-0.61	22.5	10	21.8	21.6	21.7	0.9	4.0	9
	µg/l	D2M		0.18	5.26	15	5.33	5.26	5.30	0.29	5.4	7
	µg/l	G3M		0.90	16.0	15	17.1	16.0	16.1	0.9	5.9	8
U	µg/l	A1M		-1.70	0.65	15	0.57	0.65	0.63	0.03	5.0	11
	µg/l	D2M		-0.73	0.11	25	0.10	0.11	0.11	0.01	13.6	11
	µg/l	G3M		-1.01	2.29	15	2.12	2.29	2.28	0.14	6.0	11
	mg/kg	SO4			3.61		2.72	3.61	3.39	0.59	17.4	3
V	µg/l	A1M		-1.92	4.25	10	3.84	4.03	4.05	0.14	3.3	11
	µg/l	D2M		-1.38	3.11	15	2.79	3.11	3.06	0.15	5.0	11
	µg/l	G3M		-1.14	0.88	15	0.81	0.88	0.88	0.06	7.1	9
	mg/kg	SO4			62.7		64.0	62.7	61.4	6.5	10.6	6
Zn	µg/l	A1M		0.90	33.5	10	35.0	33.0	33.0	1.6	5.0	13
	µg/l	D2M		0.46	10.2	15	10.6	10.2	10.2	0.4	3.9	12
	µg/l	G3M		-0.44	5.40	15	5.22	5.22	5.35	0.29	5.3	12
	mg/kg	SO4			203		203	203	208	11	5.5	5

Participant 17												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	s	s %	n_{stat}
Al	µg/l	A1M		0.78	335	10	348	332	331	22	6.7	16
	µg/l	D2M		3.83	37.9	15	48.8	37.6	37.9	1.5	4.0	14
	µg/l	G3M		2.03	14.3	20	17.2	14.2	14.4	1.2	8.6	12
Cr	µg/l	A1M		-1.33	4.50	15	4.05	4.40	4.40	0.22	5.0	13
	mg/kg	SN4		0.58	56.3	25	60.4	56.3	55.3	4.9	8.9	6
Drw	%	S4M		-0.24	98.1	5	97.5	98.1	98.0	0.5	0.5	10
Fe	µg/l	A1M		2.51	175	10	197	173	176	8	4.7	15
	µg/l	D2M		2.45	37.5	15	44.4	37.1	37.7	3.2	8.6	14
Hg	µg/l	A1Hg		1.87	0.15	20	0.18	0.16	0.15	0.02	9.8	10
	µg/l	D2Hg		3.20	0.075	25	0.105	0.075	0.074	0.006	8.0	7
	µg/l	G3Hg		3.20	0.050	25	0.070	0.054	0.053	0.009	16.3	8
	mg/kg	SN4			0.73		0.78	0.73	0.73	0.03	4.1	5
Mn	µg/l	D2M		-3.59	15.6	15	11.4	15.9	15.8	0.7	4.6	15

Participant 18												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	s	s %	n_{stat}
Fe	µg/l	A1M			175	10	*< 200*	173	176	8	4.7	15
	µg/l	D2M			37.5	15	*< 200*	37.1	37.7	3.2	8.6	14
	µg/l	G3M			17.5	20	*< 200*	17.4	17.6	1.6	8.9	12

Participant 19												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	s	s %	n_{stat}
Al	µg/l	A1M		0.41	335	10	342	332	331	22	6.7	16
	µg/l	D2M		0.94	37.9	15	40.6	37.6	37.9	1.5	4.0	14
As	µg/l	A1M		3.73	1.25	15	1.60	1.21	1.22	0.06	5.3	10
	µg/l	D2M		57.35	0.098	20	0.660	0.098	0.098	0.008	8.4	9
Cd	µg/l	A1M		-7.11	0.75	15	0.35	0.74	0.73	0.05	6.7	12
	µg/l	D2M		1.29	0.31	15	0.34	0.31	0.31	0.02	6.5	12
Co	µg/l	A1M		-1.51	2.25	10	2.08	2.17	2.17	0.07	3.4	11
	µg/l	D2M		-3.33	0.32	15	0.24	0.32	0.32	0.02	6.8	9
Cr	µg/l	A1M		-6.52	4.50	15	2.30	4.40	4.40	0.22	5.0	13
Cu	µg/l	A1M		-3.17	12.5	10	10.5	12.1	12.0	1.0	8.2	15
	µg/l	D2M		-0.93	56.8	15	52.9	55.8	56.9	2.9	5.2	14
Fe	µg/l	A1M		-0.47	175	10	171	173	176	8	4.7	15
	µg/l	D2M		-1.78	37.5	15	32.5	37.1	37.7	3.2	8.6	14
Mn	µg/l	A1M		-0.28	43.5	10	42.9	43.7	43.5	2.0	4.5	15
	µg/l	D2M		-0.79	15.6	15	14.7	15.9	15.8	0.7	4.6	15
Ni	µg/l	A1M		-3.14	7.25	15	5.54	7.20	7.18	0.34	4.8	12
Pb	µg/l	A1M		0.06	4.24	15	4.26	4.20	4.19	0.15	3.6	12
	µg/l	D2M		-0.80	2.18	15	2.05	2.18	2.13	0.12	5.6	12
Se	µg/l	A1M		8.43	1.25	15	2.04	1.21	1.22	0.13	10.7	10
Ti	µg/l	A1M		-1.78	22.5	10	20.5	21.6	21.7	0.9	4.0	9
	µg/l	D2M		-2.76	5.26	15	4.17	5.26	5.30	0.29	5.4	7
U	µg/l	A1M		-0.94	0.65	15	0.60	0.65	0.63	0.03	5.0	11
	µg/l	D2M		-2.55	0.11	25	0.08	0.11	0.11	0.01	13.6	11

Participant 19												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	$2\times s_{pt}$ %	Participant's result	Md	Mean	s	s %	n_{stat}
V	µg/l	A1M		-0.24	4.25	10	4.20	4.03	4.05	0.14	3.3	11
	µg/l	D2M		0.69	3.11	15	3.27	3.11	3.06	0.15	5.0	11
Zn	µg/l	A1M		-0.67	33.5	10	32.4	33.0	33.0	1.6	5.0	13
	µg/l	D2M		7.45	10.2	15	15.9	10.2	10.2	0.4	3.9	12

Participant 20												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	$2\times s_{pt}$ %	Participant's result	Md	Mean	s	s %	n_{stat}
P_{tot}	g/kg	SO4		0.54	1.11	20	1.17	1.11	1.12	0.10	9.1	6

APPENDIX 8: Summary of the z scores

Measurand	Sample	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	%
Al	A1M	S	.	Q	S	S	S	S	q	.	S	S	*q*	S	S	S	Q	S	.	*S*	.	.	.	.	75.0
	D2M	S	.	.	S	S	S	S	u	.	S	S	.	S	S	S	S	U	.	*S*	.	.	.	.	85.7
	G3M	S	.	.	S	S	S	S	u	.	S	S	.	S	S	S	S	Q	.	.	.	.	.	.	84.6
	SO4	*S*	.	S	*q*	S	.	S	.	.	.	.	.	.	.	.	S	.	.	.	.	.	.	.	83.3
As	A1M	S	.	.	S	S	.	S	*S*	.	.	S	.	S	S	S	S	.	.	*U*	.	.	.	.	90.9
	D2M	.	.	.	S	S	.	S	*S*	.	.	S	.	S	S	S	S	.	.	*U*	.	.	.	.	90.0
	G3M	.	.	.	q	S	.	S	*S*	.	.	S	.	S	S	S	U	.	.	.	.	.	.	.	77.8
	SO4	S	.	S	S	S	.	S	.	.	.	.	.	.	.	.	S	.	.	.	.	.	.	.	100
Cd	A1M	S	.	.	S	S	S	S	*S*	.	S	S	u	S	S	S	q	.	.	*u*	.	.	.	.	78.6
	D2M	S	.	.	S	S	S	S	*S*	.	.	S	.	S	S	S	q	.	.	*S*	.	.	.	.	91.7
	G3M	U	.	.	S	S	S	S	*S*	.	.	S	.	S	S	S	S	.	.	.	.	.	.	.	90.9
Co	A1M	S	.	U	S	S	.	S	.	.	S	S	.	S	S	S	S	.	.	*S*	.	.	.	.	91.7
	D2M	S	.	.	S	S	.	S	.	.	.	S	.	S	S	S	S	.	.	*u*	.	.	.	.	90.0
	G3M	.	.	.	S	S	.	S	.	.	.	S	.	S	S	S	q	.	.	.	.	.	.	.	87.5
	SO4	S	.	*S*	S	S	.	S	.	.	.	.	.	.	.	.	S	.	.	.	.	.	.	.	100
Cr	A1M	S	.	.	S	S	.	S	*S*	.	S	S	S	S	S	S	S	S	.	*u*	.	.	.	.	92.9
	D2M	S	.	.	S	S	.	S	*S*	.	S	S	.	S	S	U	S	.	.	.	.	.	.	.	90.9
	G3M	.	.	.	S	S	.	S	*S*	.	.	S	.	S	S	S	S	.	.	.	.	.	.	.	100
	SN4	.	.	.	.	S	.	.	.	.	.	S	.	S	S	S	.	S	.	.	.	.	.	.	100
	SO4	S	.	S	S	S	.	S	.	.	.	.	.	.	.	.	S	.	.	.	.	.	.	.	100
Cu	A1M	S	.	S	u	S	S	S	*S*	.	S	S	*u*	S	S	S	S	.	.	*u*	.	.	.	.	80.0
	D2M	S	.	S	S	S	S	S	*S*	.	S	S	.	S	S	S	S	.	.	*S*	.	.	.	.	100
	G3M	S	.	.	S	S	S	S	*S*	.	S	S	.	S	S	S	S	.	.	.	.	.	.	.	100
	SN4	.	.	.	.	S	.	.	*S*	.	.	S	.	S	S	S	.	.	.	.	.	.	.	.	100
	SO4	S	.	S	S	S	.	S	.	.	.	.	.	.	.	.	S	.	.	.	.	.	.	.	100
Drw	S4M	S	.	S	*S*	*S*	.	S	.	.	.	S	S	S	S	S	.	*S*	.	.	.	.	.	.	100
Fe	A1M	S	.	S	S	S	S	S	u	.	S	S	S	S	S	S	S	Q	.	*S*	.	.	.	.	87.5
	D2M	S	.	S	S	S	S	S	q	.	S	S	.	S	S	S	S	Q	.	*S*	.	.	.	.	86.7
	G3M	S	.	S	S	S	*S*	S	u	.	S	S	.	S	S	S	S	.	.	.	.	.	.	.	92.3
	SN4	.	.	.	.	*S*	.	.	*Q*	.	.	S	.	S	S	S	.	.	.	.	.	.	.	.	83.3
	SO4	*S*	.	S	*S*	*S*	.	S	.	.	.	.	.	.	.	.	S	.	.	.	.	.	.	.	100
Hg	A1Hg	S	.	u	S	S	.	S	U	.	.	S	S	S	S	S	S	S	.	.	.	.	.	.	84.6
	D2Hg	.	.	.	Q	S	.	S	U	.	.	S	.	S	S	S	S	U	.	.	.	.	.	.	70.0
	G3Hg	.	.	.	U	S	.	S	U	.	.	S	.	S	S	S	S	U	.	.	.	.	.	.	70.0
	SO4	*u*	.	S	S	S	.	S	.	.	.	.	S	.	.	.	S	.	.	.	.	.	.	.	85.7
Mn	A1M	S	.	S	S	S	S	S	S	.	S	S	S	S	S	S	S	.	.	S	.	.	.	.	100
	D2M	S	.	S	u	S	S	S	S	.	S	S	.	S	S	S	S	u	.	*S*	.	.	.	.	86.7
	G3M	S	.	.	S	S	S	S	S	.	S	S	.	S	S	S	S	.	.	.	.	.	.	.	100
	SN4	.	.	.	.	S	.	.	*S*	.	.	S	.	S	S	S	.	.	.	.	.	.	.	.	100
	SO4	*S*	.	S	*S*	*S*	.	S	.	.	.	.	.	.	.	.	S	.	.	.	.	.	.	.	100
Ni	A1M	S	.	S	S	S	.	S	*S*	.	S	S	S	S	S	S	S	.	.	*u*	.	.	.	.	92.9
	D2M	.	.	.	S	S	.	Q	*S*	.	.	S	.	S	S	*U*	S	.	.	.	.	.	.	.	77.8
	G3M	S	.	.	U	S	.	S	*S*	.	U	S	.	S	S	S	S	.	.	.	.	.	.	.	81.8
	SO4	S	.	S	S	S	.	S	.	.	.	.	.	.	.	.	S	.	.	.	.	.	.	.	100
Pb	A1M	S	.	.	S	S	S	S	*S*	.	Q	S	.	S	S	S	S	.	.	*S*	.	.	.	.	92.3
	D2M	S	.	.	S	S	S	S	*S*	.	.	S	.	S	S	S	S	.	.	*S*	.	.	.	.	100
	G3M	S	.	.	S	S	S	S	*S*	.	.	S	.	S	S	S	q	.	.	.	.	.	.	.	90.9
	SO4	S	.	S	S	S	.	S	.	.	.	.	.	.	.	.	S	.	.	.	.	.	.	.	100

Measurand	Sample	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	%
P_{tot}	SN4	.	.	.	.	*S*	.	.	*S*	S	.	*S*	.	S	S	S	.	.	.	.	.	.	.	.	100
	SO4	*S*	.	*S*	*S*	.	.	S	.	.	.	.	.	.	.	.	S	.	.	.	S	.	.	.	100
Se	A1M	S	.	.	S	S	.	S	S	.	.	S	.	S	S	S	u	.	.	*U*	.	.	.	.	81.8
	D2M	.	.	.	S	S	.	S	*S*	.	.	S	.	S	S	S	S	.	.	.	.	.	.	.	100
	G3M	S	.	.	S	S	.	S	*S*	.	.	S	.	S	S	S	q	.	.	.	.	.	.	.	90.0
Ti	A1M	*S*	.	.	*S*	*S*	.	.	.	.	*S*	*S*	.	.	S	S	S	.	.	*S*	.	.	.	.	100
	D2M	.	.	.	*S*	*S*	.	.	.	.	*S*	*S*	.	.	S	S	S	.	.	*q*	.	.	.	.	87.5
	G3M	*S*	.	.	*S*	*S*	.	.	.	.	*S*	*S*	.	.	S	S	S	.	.	.	.	.	.	.	100
U	A1M	S	S	.	S	S	.	S	*S*	.	.	U	.	S	S	S	S	.	.	*S*	.	.	.	.	91.7
	D2M	.	S	.	S	S	.	S	*S*	.	.	S	.	S	S	S	S	.	.	*q*	.	.	.	.	90.9
	G3M	S	S	.	S	S	.	S	*S*	.	.	S	.	S	S	S	S	.	.	.	.	.	.	.	100
V	A1M	S	.	.	S	S	.	S	.	.	*S*	S	.	S	S	S	S	.	.	*S*	.	.	.	.	100
	D2M	S	.	.	S	S	.	S	.	.	*S*	S	.	S	S	S	S	.	.	*S*	.	.	.	.	100
	G3M	S	.	.	S	S	.	S	.	.	.	S	.	S	S	S	S	.	.	.	.	.	.	.	100
Zn	A1M	S	.	S	u	S	S	S	*u*	.	S	S	q	S	S	S	S	.	.	*S*	.	.	.	.	80.0
	D2M	S	.	S	S	S	S	S	.	.	S	S	.	S	S	S	S	.	.	*U*	.	.	.	.	92.3
	G3M	S	.	S	S	S	S	S	.	.	S	S	.	S	S	U	S	.	.	.	.	.	.	.	91.7
	SN4	.	.	.	.	S	.	.	*S*	.	.	S	.	S	S	S	.	.	.	.	.	.	.	.	100
%		96	100	88	87	100	100	98	74	100	93	98	64	100	100	95	86	42		59	100				
accredited		43	3	24	51	56	20	56	12	1	21	51	1	52	55	48	59	11			1				

S - satisfactory (-2 ≤ z ≤ 2), Q - questionable (2 < z < 3), q - questionable (-3 < z < -2),
U - unsatisfactory (z ≥ 3), and u - unsatisfactory (z ≤ -3), respectively
bold - accredited, italics - non-accredited, normal - unknown
% - percentage of satisfactory results

Totally satisfactory, % in all: 91 % in accredited: 93 % in non-accredited: 82

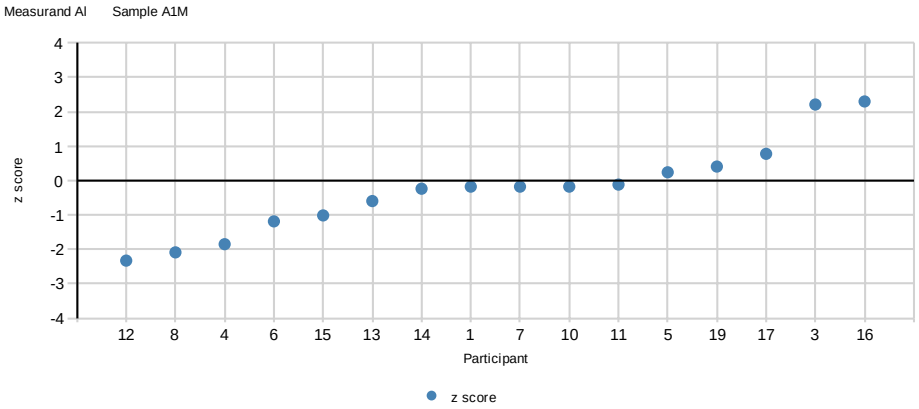
APPENDIX 9: Summary of the E_n scores

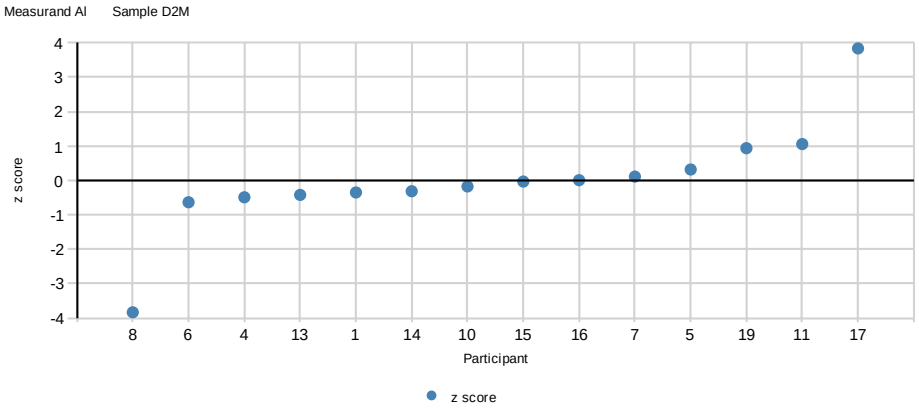
Measurand	Sample	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	%
Al	SN4	.	.	.	.	0.1	.	.	.	.	.	-0.1	.	.	0.2	-1.2	.	.	.	.	.	.	.	.	75.0
As	SN4	.	.	.	.	0.0	.	.	.	.	.	0.0	.	0.3	-0.2	-1.1	.	.	.	.	.	.	.	.	80.0
Cd	SN4	.	.	.	.	0.2	.	.	.	.	.	-0.3	.	0.0	-0.2	1.1	.	.	.	.	.	.	.	.	80.0
	SO4	-1.1	.	-0.2	0.1	0.5	.	0.3	.	.	.	.	.	.	.	.	-0.7	.	.	.	.	.	.	.	83.3
Co	SN4	.	.	.	.	0.0	.	.	.	.	.	0.2	.	0.3	-0.5	0.0	.	.	.	.	.	.	.	.	100
Hg	SN4	.	.	.	.	0.0	.	.	.	.	.	0.0	.	-0.2	.	-0.1	.	0.3	.	.	.	.	.	.	100
Ni	SN4	.	.	.	.	0.0	.	.	.	.	.	0.1	.	0.0	-0.3	-0.4	.	.	.	.	.	.	.	.	100
N_{tot}	SN4	.	.	.	.	.	.	.	.	0.0	.	.	.	-0.7	-4.3	-0.6	.	.	.	.	.	.	.	.	75.0
Pb	SN4	.	.	.	.	0.0	.	.	.	.	.	-0.2	.	0.0	-0.5	0.4	.	.	.	.	.	.	.	.	100
Se	SN4	.	.	.	.	-0.1	.	.	.	.	.	1.0	.	0.1	-0.6	0.5	.	.	.	.	.	.	.	.	80.0
S_{tot}	SN4	.	.	.	.	-0.8	.	.	.	.	.	0.2	.	0.1	-0.1	.	.	.	.	.	.	.	.	.	100
	SO4	.	.	.	0.1	.	.	0.8	.	.	.	.	.	.	.	.	-0.1	.	.	.	.	.	.	.	100
TC	S4M	0.5	.	0.1	.	.	.	.	.	-0.6	.	.	.	.	0.0	.	.	.	.	.	.	.	.	.	100
U	SN4	.	-0.6	.	.	0.6	.	.	.	.	.	0.0	.	.	0.0	0.0	.	.	.	.	.	.	.	.	100
	SO4	.	.	.	.	0.2	.	.	.	.	.	.	.	.	.	.	-1.0	.	.	.	.	.	.	.	100
V	SN4	.	.	.	.	0.1	.	.	.	.	.	0.0	.	-0.5	0.0	-1.1	.	.	.	.	.	.	.	.	80.0
	SO4	-0.1	.	0.1	-1.2	0.3	.	-0.1	.	.	.	.	.	.	.	.	0.1	.	.	.	.	.	.	.	83.3
%		67	100	100	67	100		100		100		100		100	100	64	75	100							

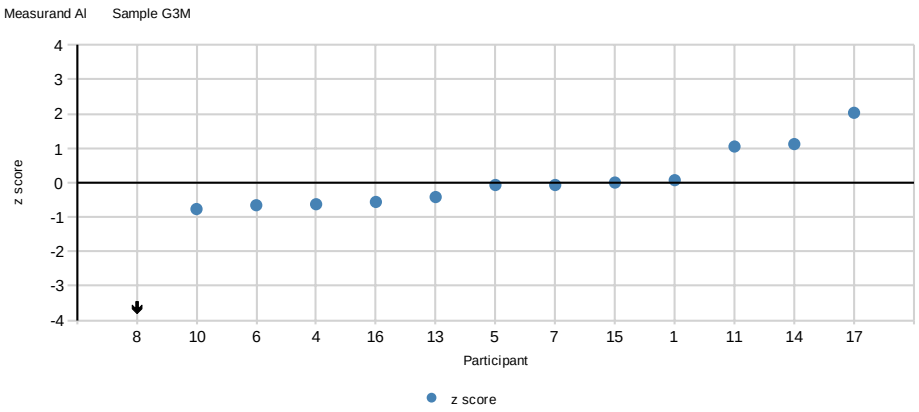
***E_n* scores enable to estimate the proximity of participant results to the assigned value taking into consideration their reported expanded uncertainty**
Scores of $-1.0 < E_n < 1.0$ indicate successful performance
Scores of $E_n \geq 1.0$ or $E_n \leq -1.0$ indicate a need to review the uncertainty estimated or to correct a measurement issue

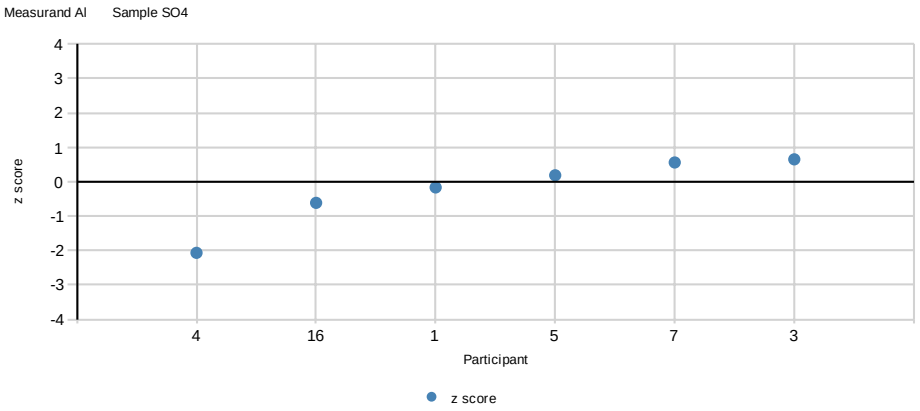
Totally satisfactory, % in all: 90

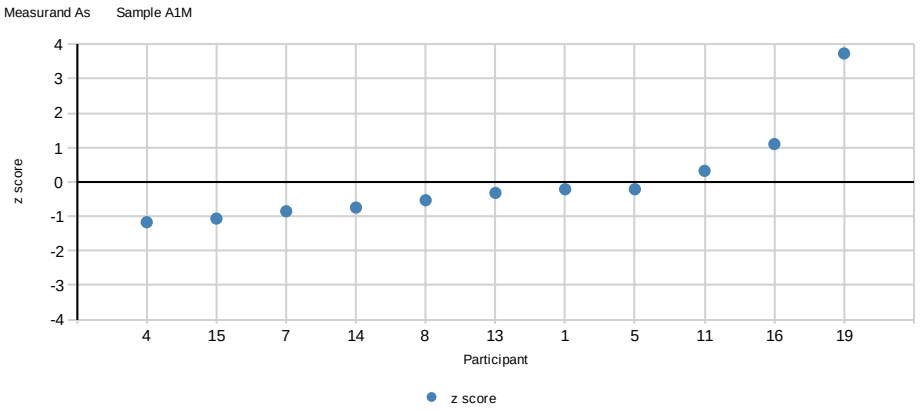
APPENDIX 10: z scores in ascending order

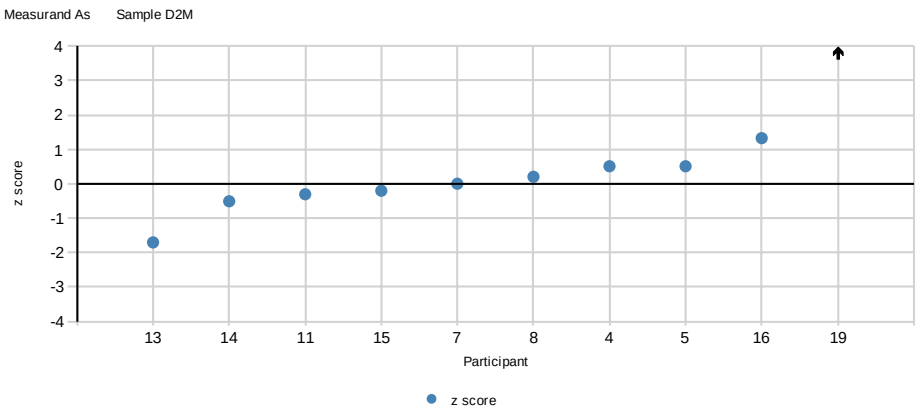




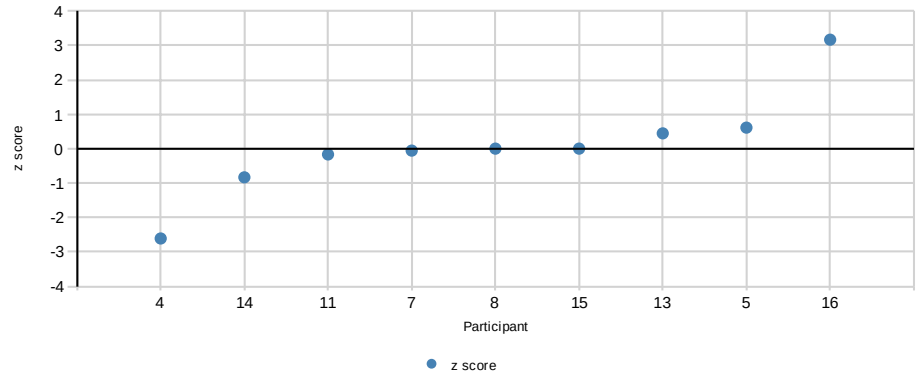



Measurand Al Sample SO4
z score
4
3
2
1
0
-1
-2
-3
-4
4
16
1
5
7
3
Participant
z score

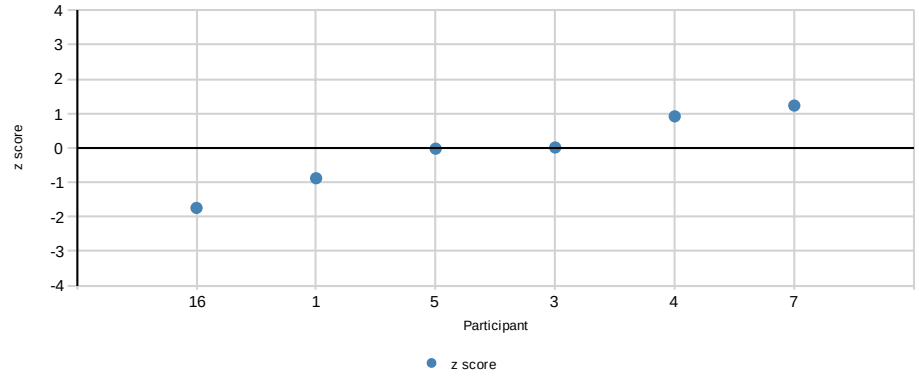

Measurand As Sample A1M
z score
4
3
2
1
0
-1
-2
-3
-4
4
15
7
14
8
13
1
5
11
16
19
Participant
z score


Measurand As Sample D2M
z score
4
3
2
1
0
-1
-2
-3
-4
13
14
11
15
7
8
4
5
16
19
Participant
z score

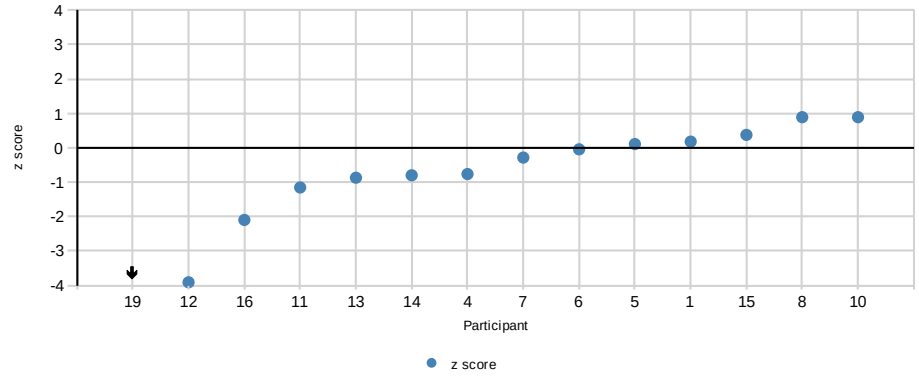
Measurand As Sample G3M

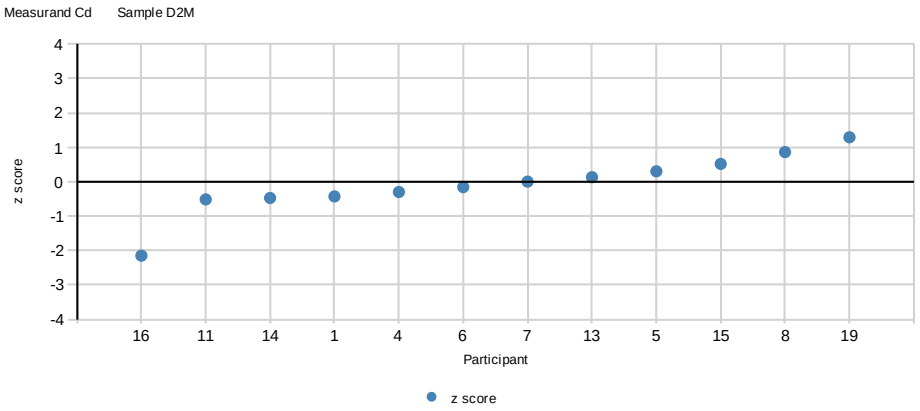


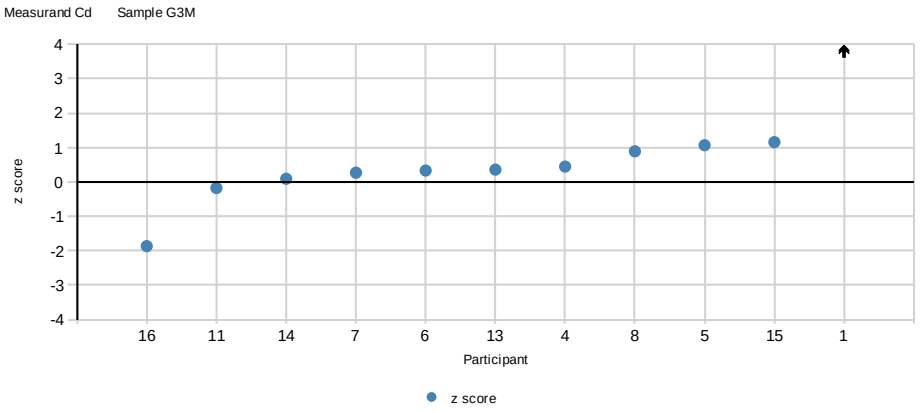
Measurand As Sample SO4

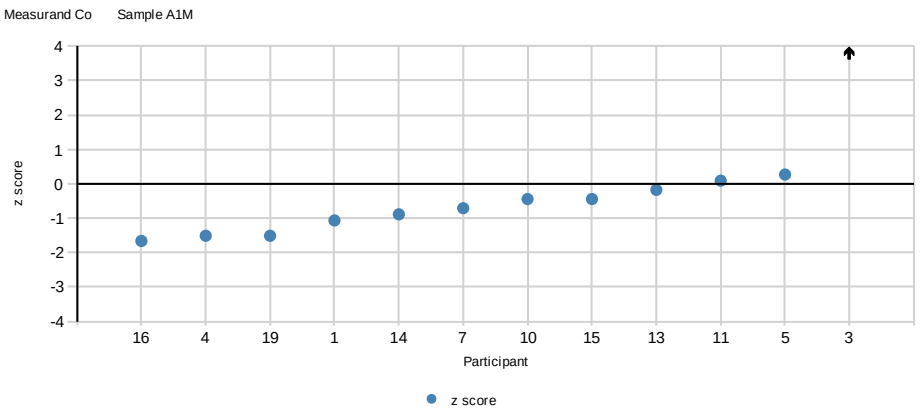


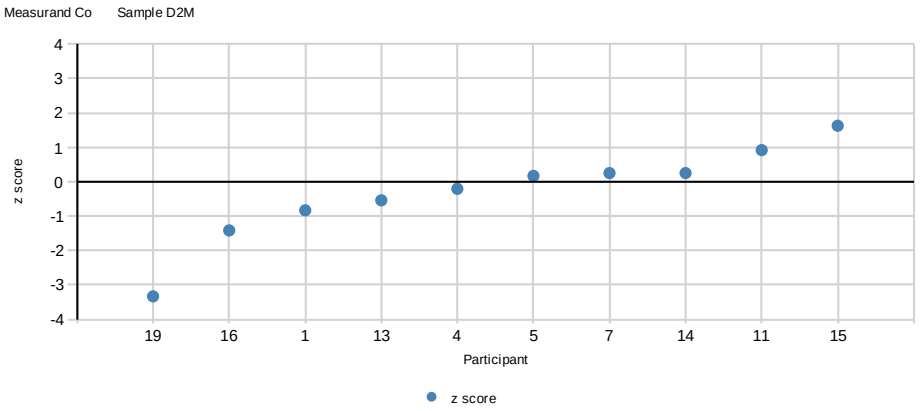
Measurand Cd Sample A1M

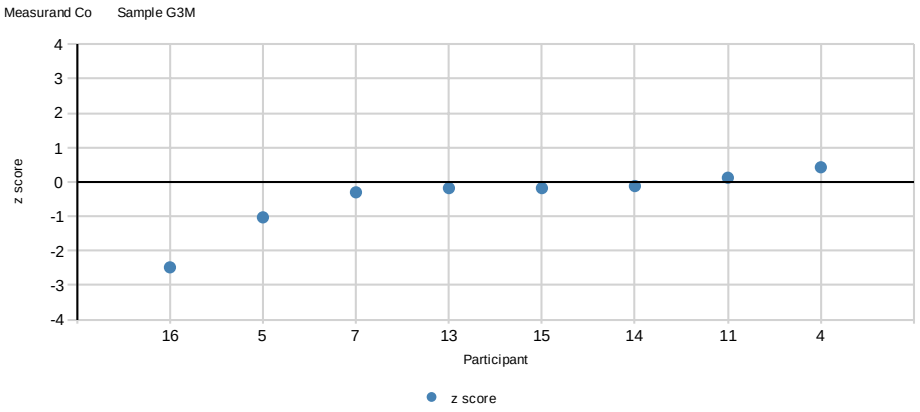


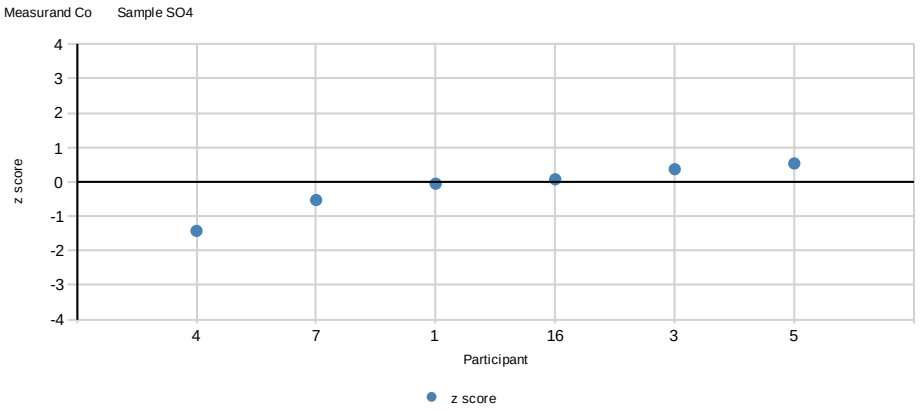

Measurand Cd Sample D2M
z score
4
3
2
1
0
-1
-2
-3
-4
16 11 14 1 4 6 7 13 5 15 8 19
Participant
z score

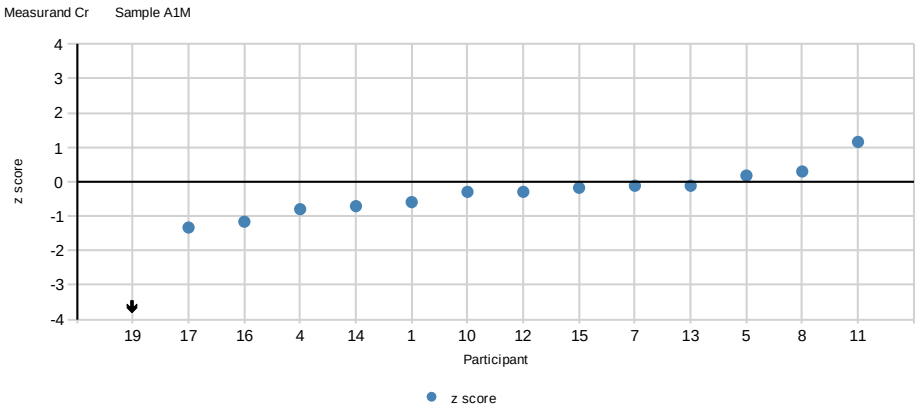

Measurand Cd Sample G3M
z score
4
3
2
1
0
-1
-2
-3
-4
16 11 14 7 6 13 4 8 5 15 1
Participant
z score

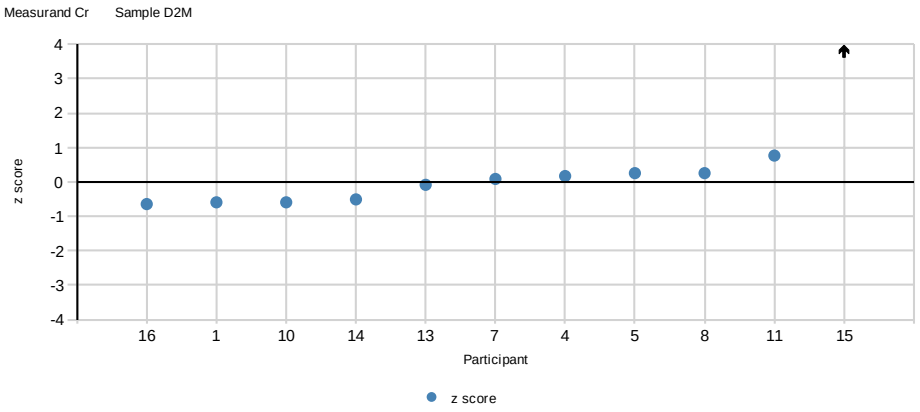

Measurand Co Sample A1M
z score
4
3
2
1
0
-1
-2
-3
-4
16 4 19 1 14 7 10 15 13 11 5 3
Participant
z score

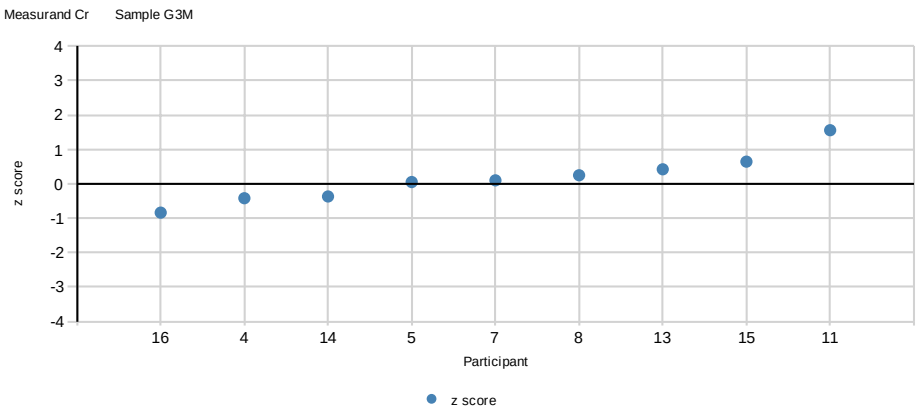

Measurand Co
Sample D2M
z score
4
3
2
1
0
-1
-2
-3
-4
19
16
1
13
4
5
7
14
11
15
Participant
z score


Measurand Co
Sample G3M
z score
4
3
2
1
0
-1
-2
-3
-4
16
5
7
13
15
14
11
4
Participant
z score

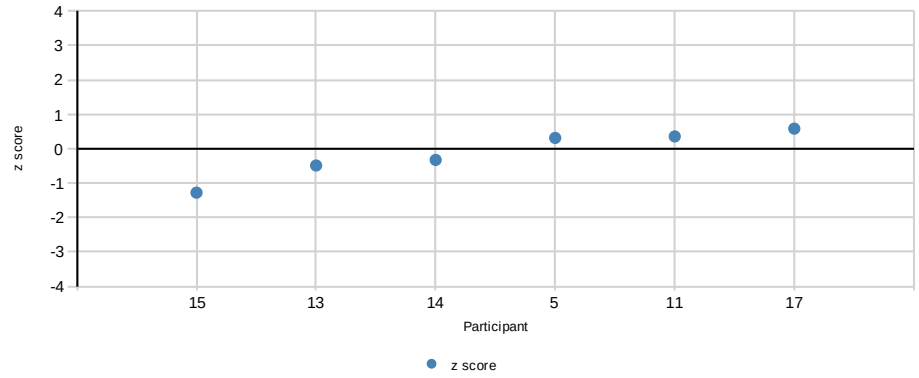

Measurand Co
Sample SO4
z score
4
3
2
1
0
-1
-2
-3
-4
4
7
1
16
3
5
Participant
z score


Measurand Cr Sample A1M
z score
4
3
2
1
0
-1
-2
-3
-4
19 17 16 4 14 1 10 12 15 7 13 5 8 11
Participant
z score

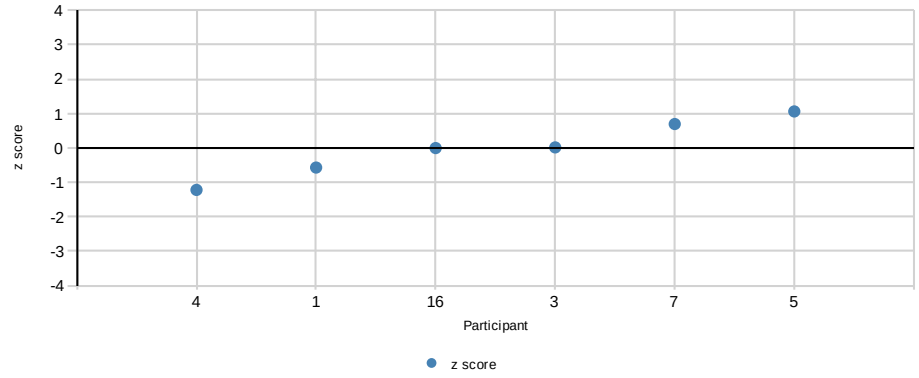

Measurand Cr Sample D2M
z score
4
3
2
1
0
-1
-2
-3
-4
16 1 10 14 13 7 4 5 8 11 15
Participant
z score


Measurand Cr Sample G3M
z score
4
3
2
1
0
-1
-2
-3
-4
16 4 14 5 7 8 13 15 11
Participant
z score

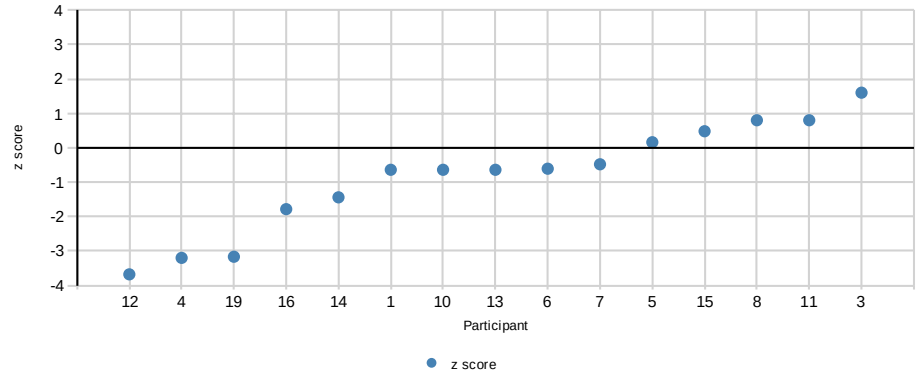
Measurand Cr Sample SN4

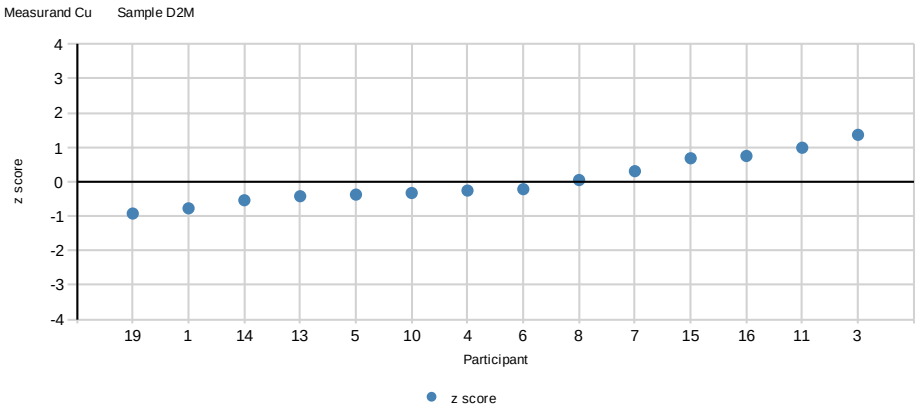


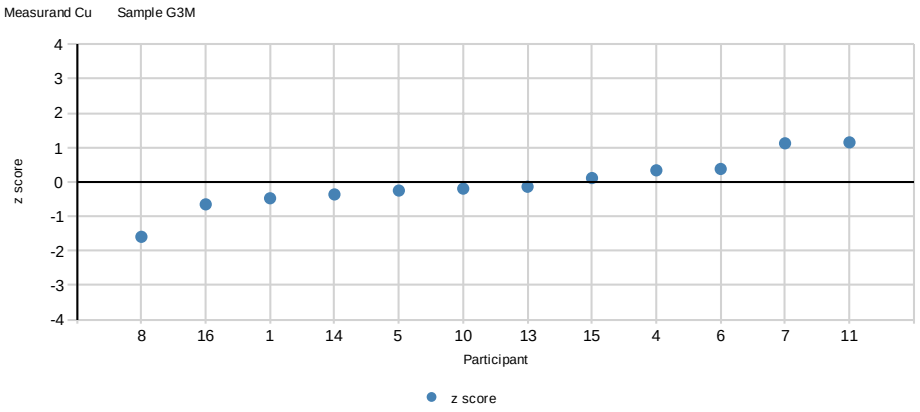
Measurand Cr Sample SO4

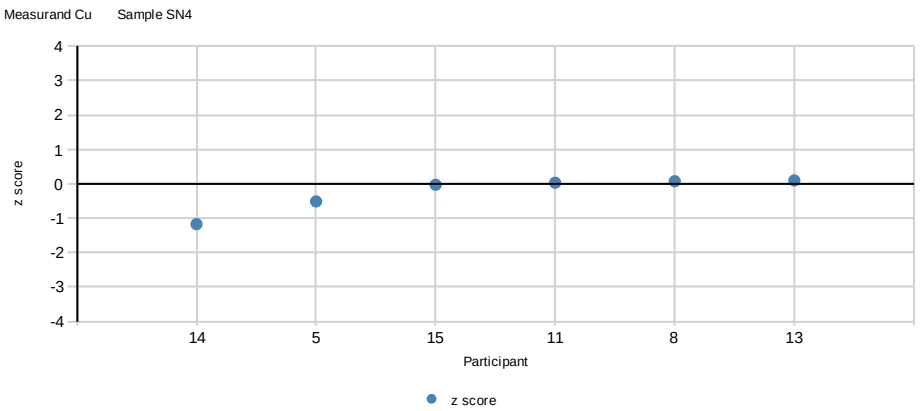


Measurand Cu Sample A1M

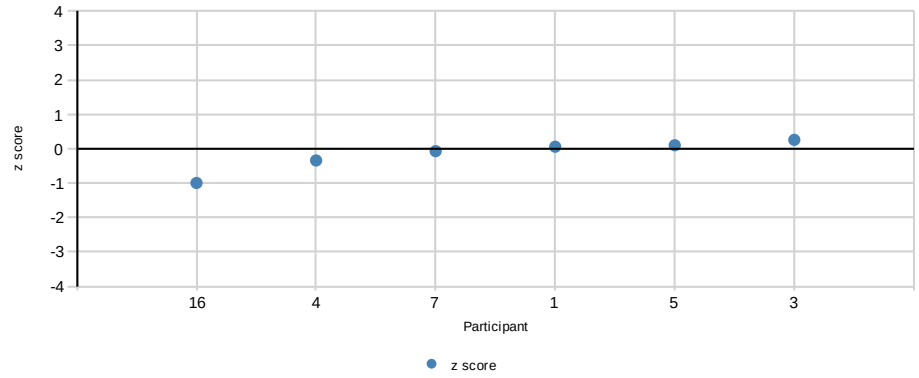



Measurand Cu Sample D2M
z score
4
3
2
1
0
-1
-2
-3
-4
19 1 14 13 5 10 4 6 8 7 15 16 11 3
Participant
z score

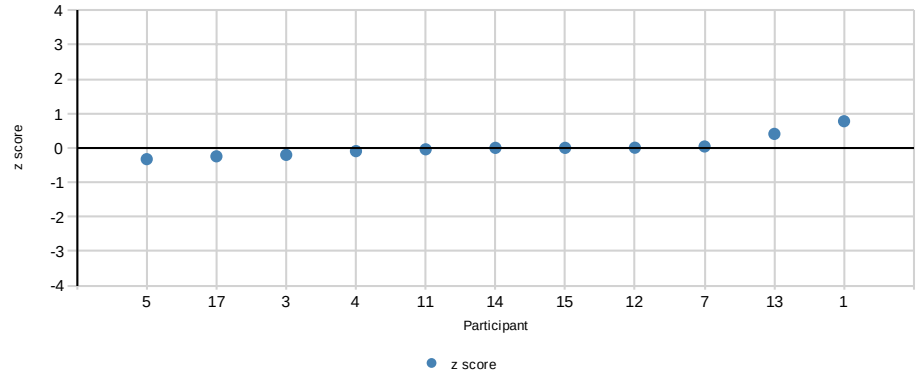

Measurand Cu Sample G3M
z score
4
3
2
1
0
-1
-2
-3
-4
8 16 1 14 5 10 13 15 4 6 7 11
Participant
z score


Measurand Cu Sample SN4
z score
4
3
2
1
0
-1
-2
-3
-4
14 5 15 11 8 13
Participant
z score

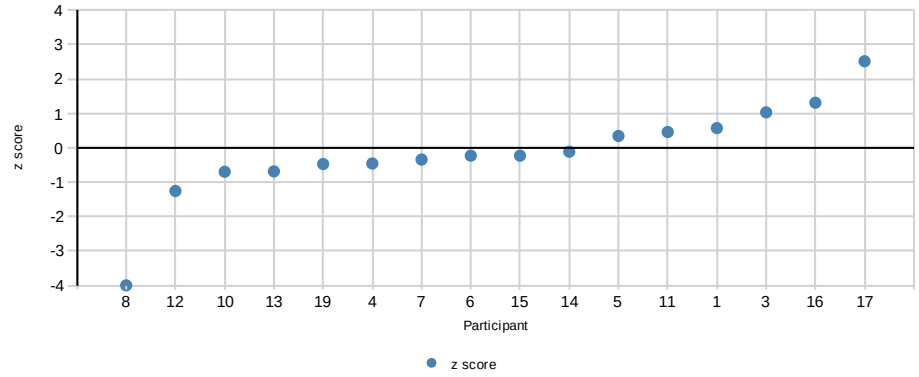
Measurand Cu Sample SO4

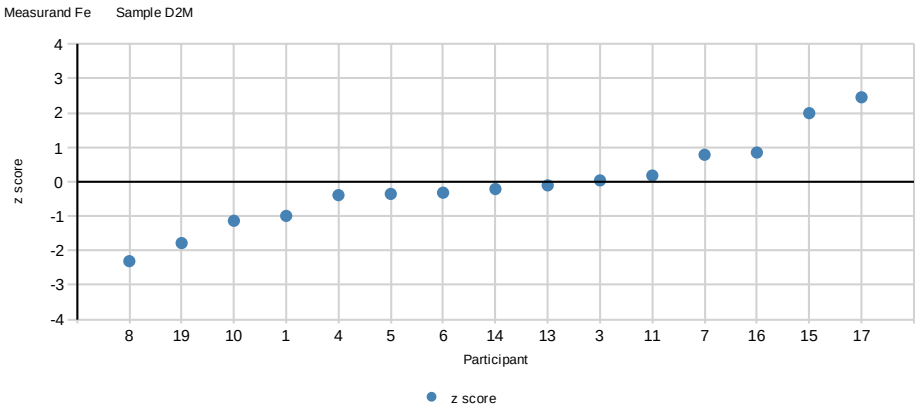


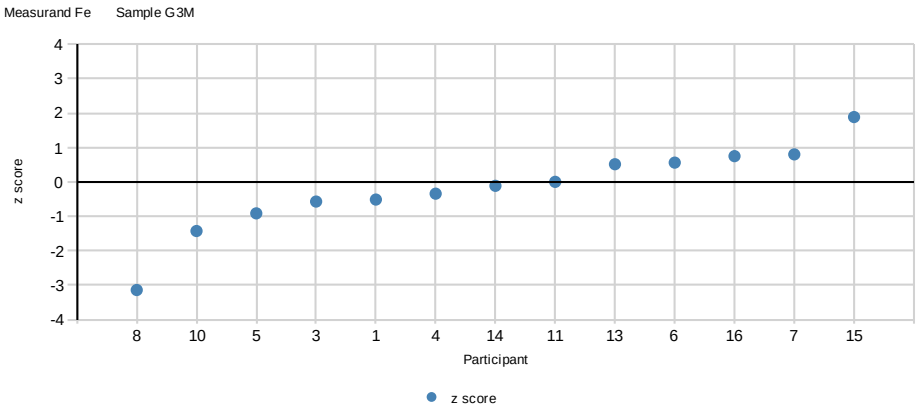
Measurand Drw Sample S4M

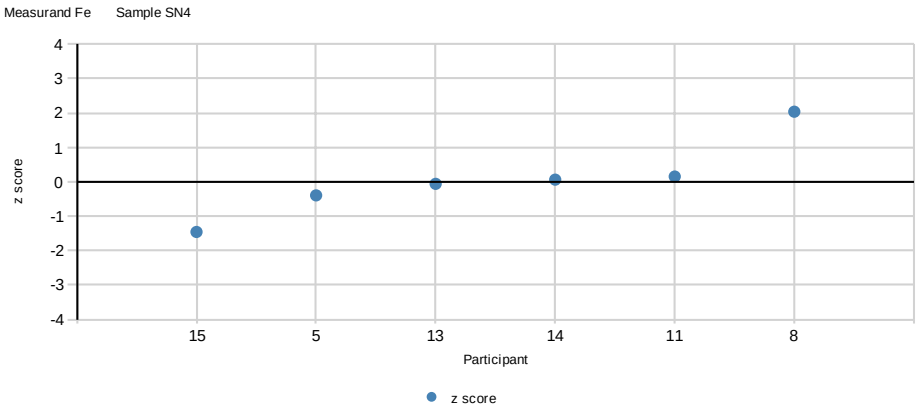


Measurand Fe Sample A1M

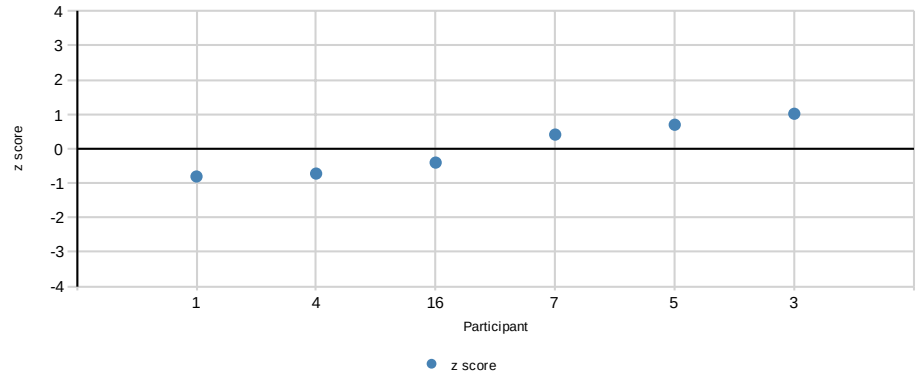



Measurand Fe Sample D2M
z score
4
3
2
1
0
-1
-2
-3
-4
8 19 10 1 4 5 6 14 13 3 11 7 16 15 17
Participant
z score

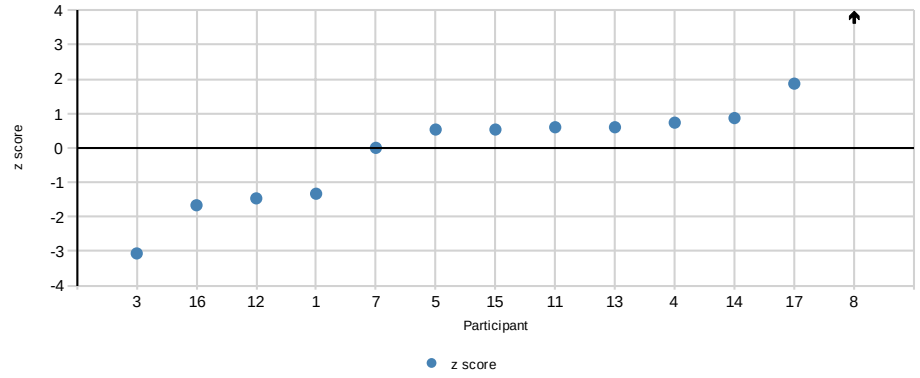

Measurand Fe Sample G3M
z score
4
3
2
1
0
-1
-2
-3
-4
8 10 5 3 1 4 14 11 13 6 16 7 15
Participant
z score


Measurand Fe Sample SN4
z score
4
3
2
1
0
-1
-2
-3
-4
15 5 13 14 11 8
Participant
z score

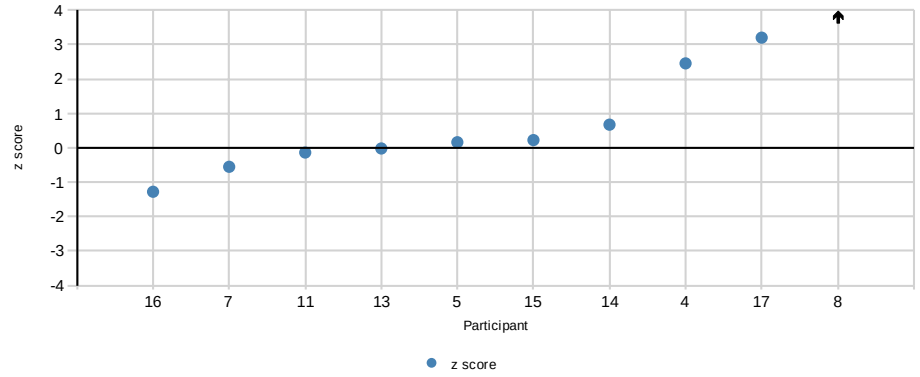
Measurand Fe Sample SO4

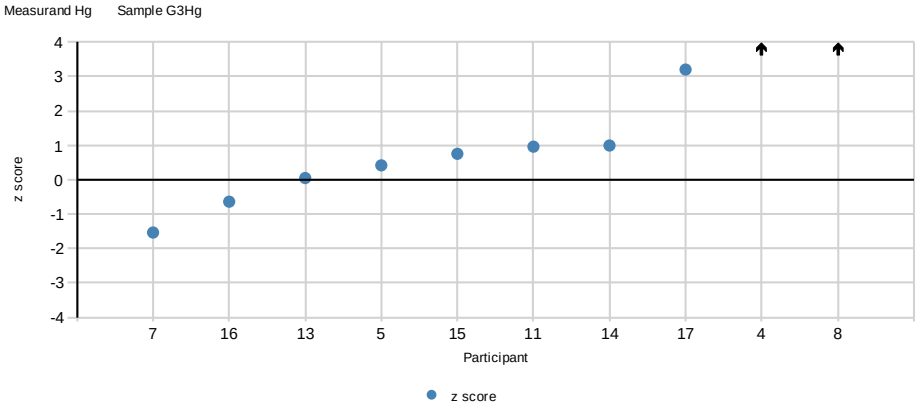


Measurand Hg Sample A1Hg



Measurand Hg Sample D2Hg




Measurand Hg Sample G3Hg
z score
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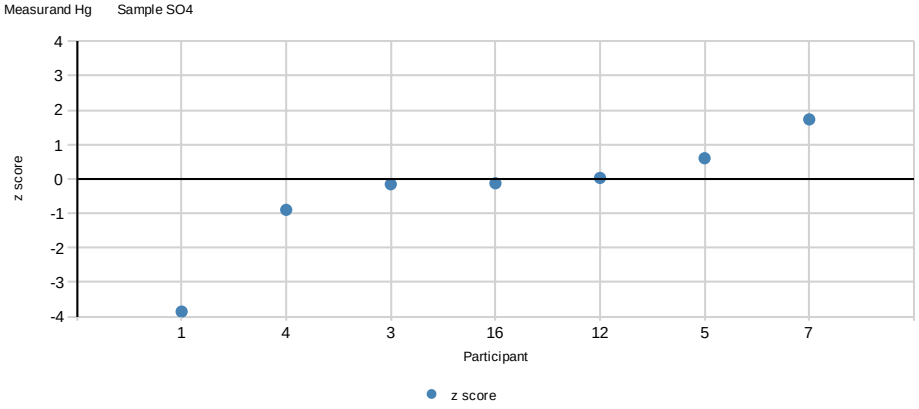
3
2
1
0
-1
-2
-3
-4
7 16 13 5 15 11 14 17 4 8
Participant
z score


Measurand Hg Sample SO4
z score
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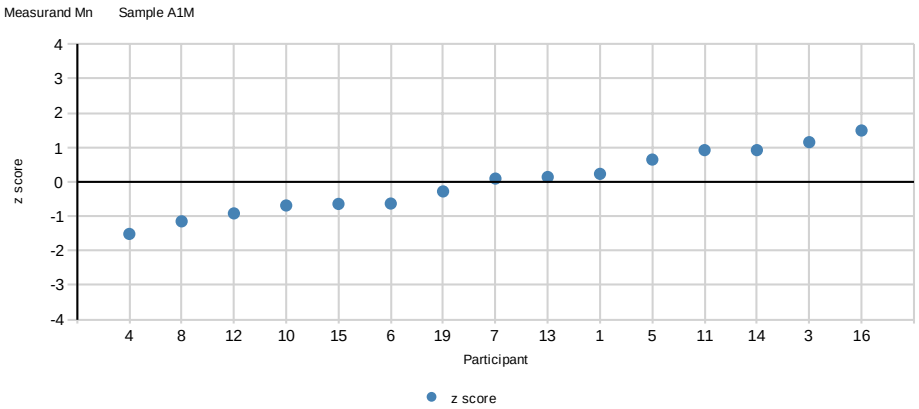
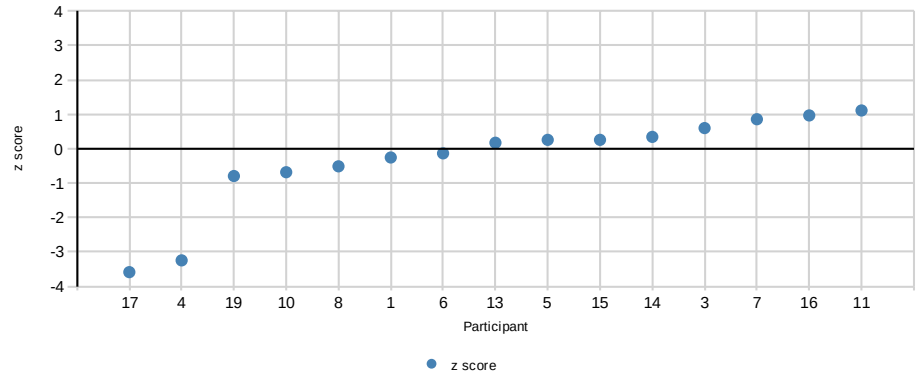
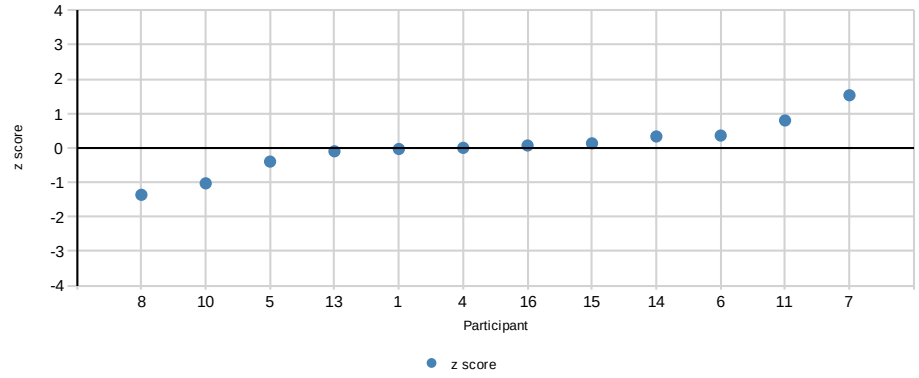
3
2
1
0
-1
-2
-3
-4
1 4 3 16 12 5 7
Participant
z score


Measurand Mn Sample A1M
z score
4
3
2
1
0
-1
-2
-3
-4
4 8 12 10 15 6 19 7 13 1 5 11 14 3 16
Participant
z score

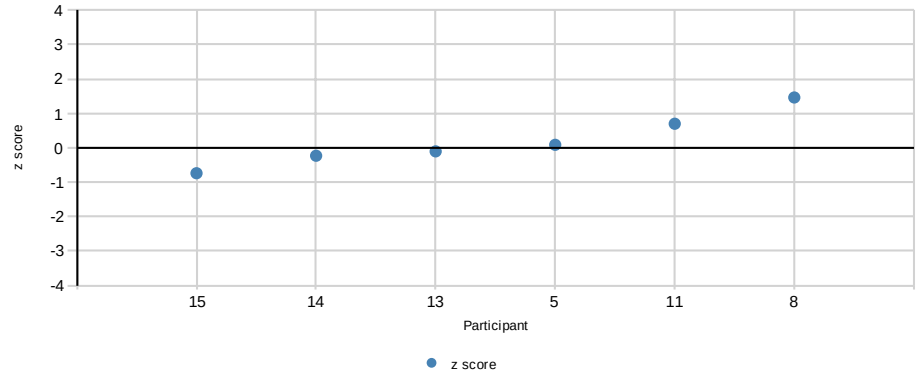
Measurand Mn Sample D2M

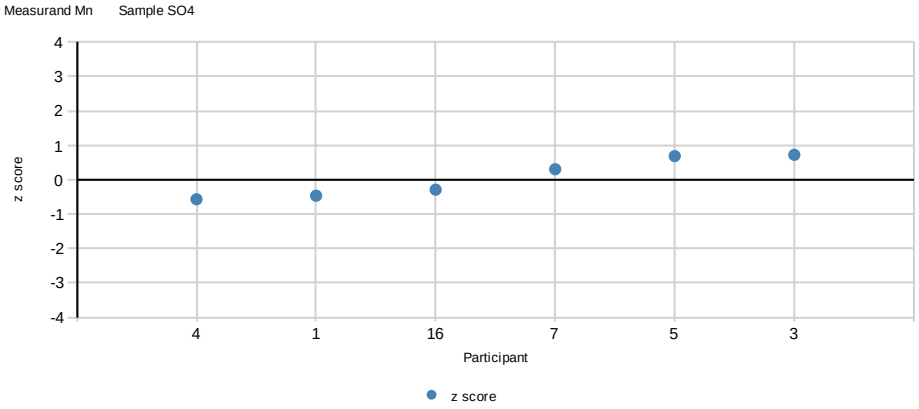


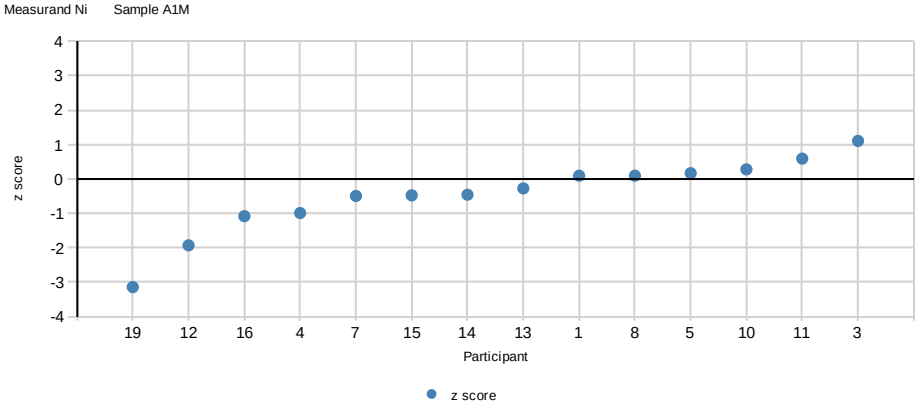
Measurand Mn Sample G3M



Measurand Mn Sample SN4




Measurand Mn Sample SO4
z score
4
3
2
1
0
-1
-2
-3
-4
4 1 16 7 5 3
Participant
z score


Measurand Ni Sample A1M
z score
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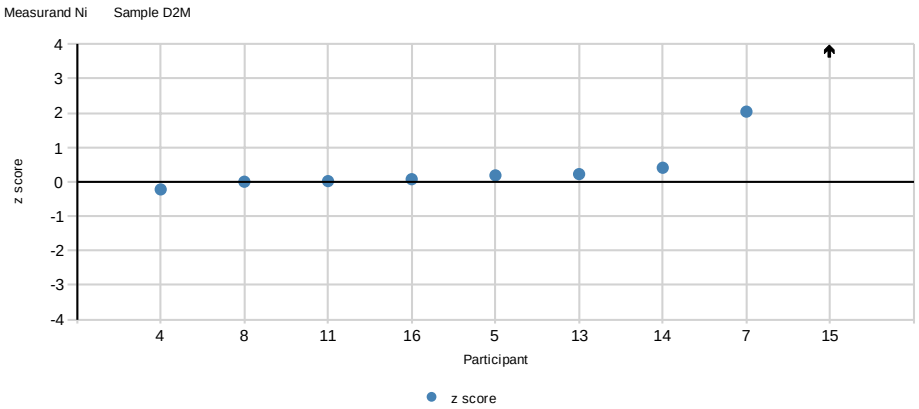
1
0
-1
-2
-3
-4
19 12 16 4 7 15 14 13 1 8 5 10 11 3
Participant
z score


Measurand Ni Sample D2M
z score
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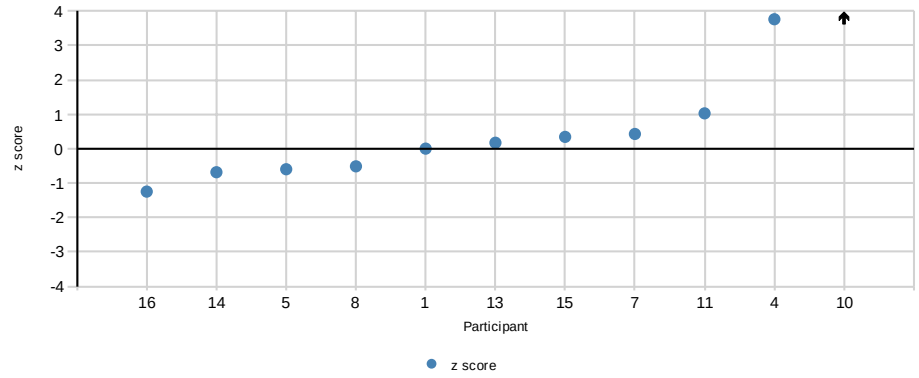
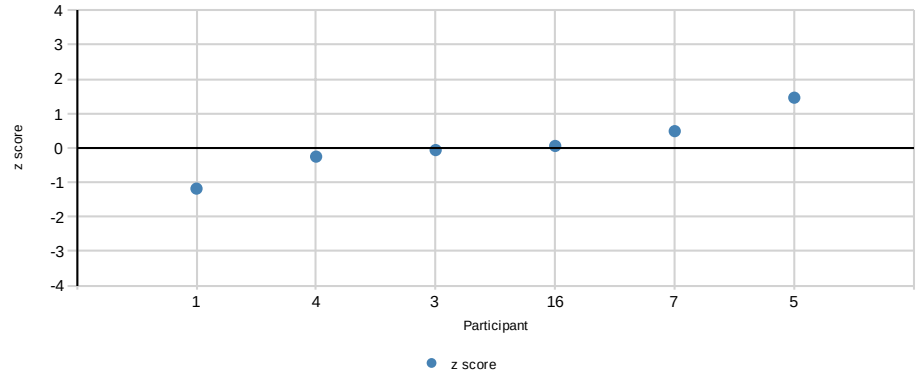
3
2
1
0
-1
-2
-3
-4
4 8 11 16 5 13 14 7 15
Participant
z score

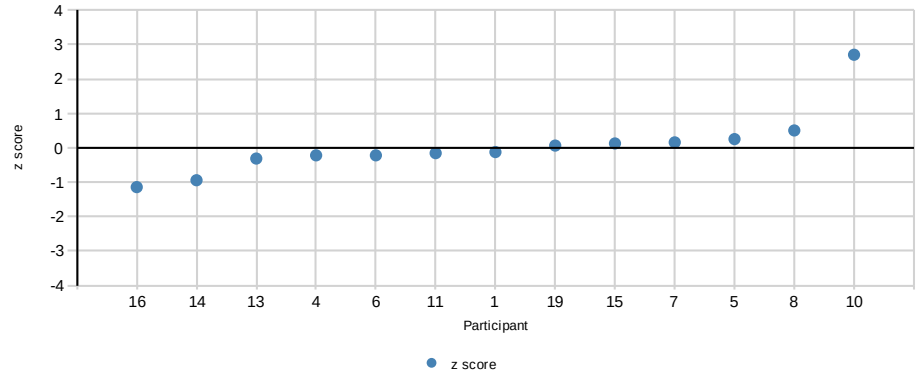
Measurand Ni Sample G3M

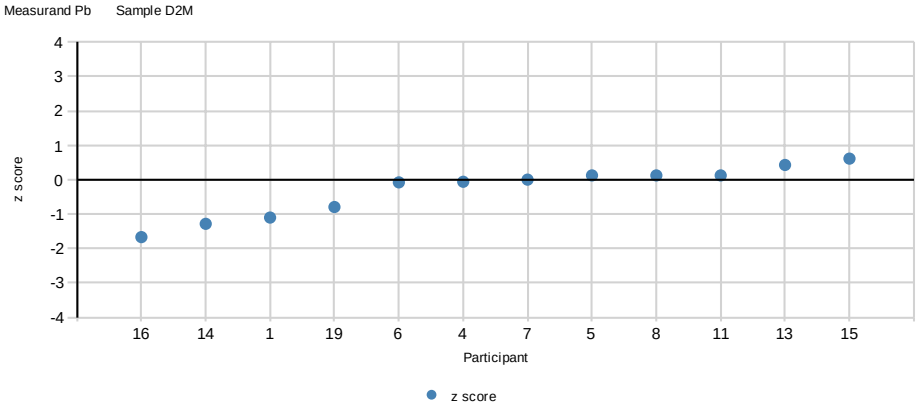


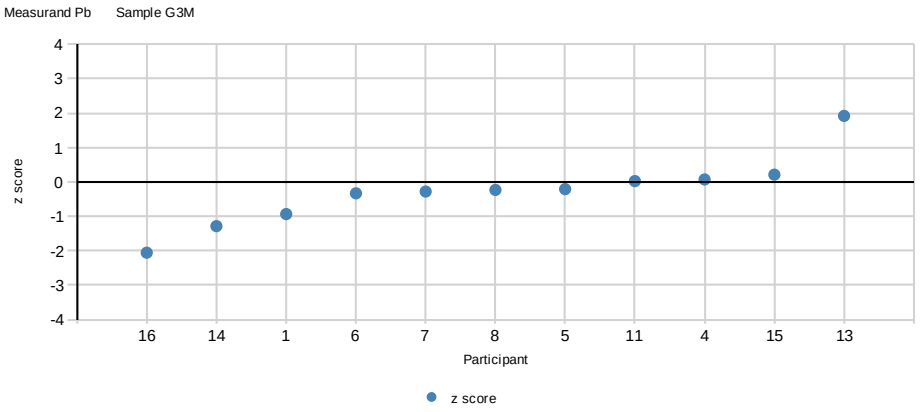
Measurand Ni Sample SO4

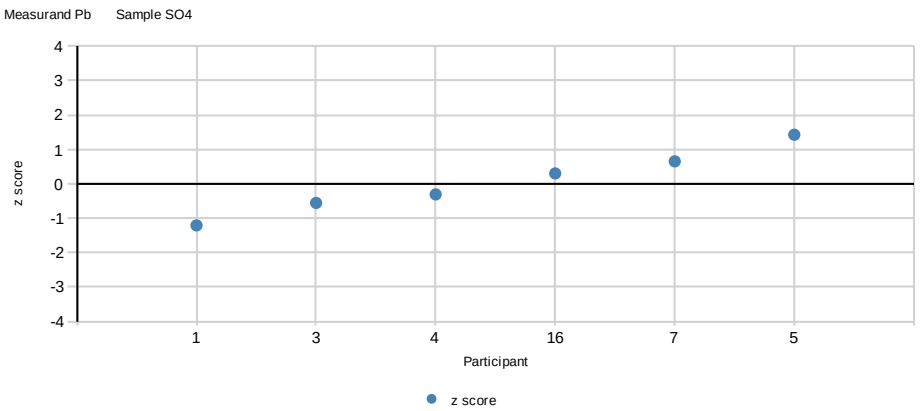


Measurand Pb Sample A1M




Measurand Pb Sample D2M
z score
4
3
2
1
0
-1
-2
-3
-4
16 14 1 19 6 4 7 5 8 11 13 15
Participant
z score


Measurand Pb Sample G3M
z score
4
3
2
1
0
-1
-2
-3
-4
16 14 1 6 7 8 5 11 4 15 13
Participant
z score


Measurand Pb Sample SO4
z score
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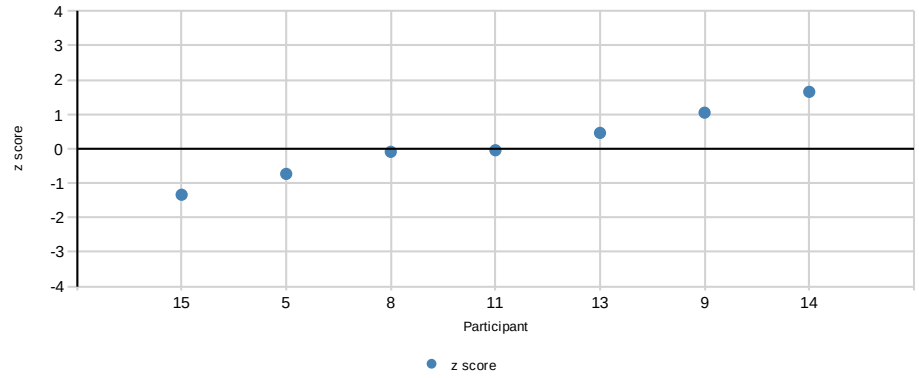
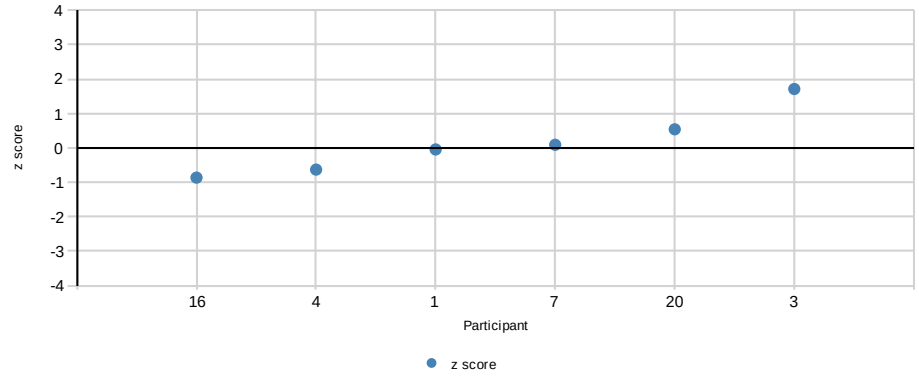
3
2
1
0
-1
-2
-3
-4
1 3 4 16 7 5
Participant
z score

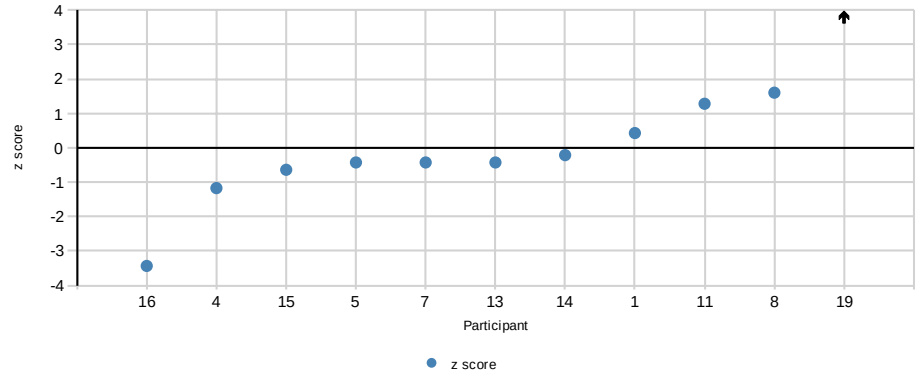
Measurand P_{tot} Sample SN4



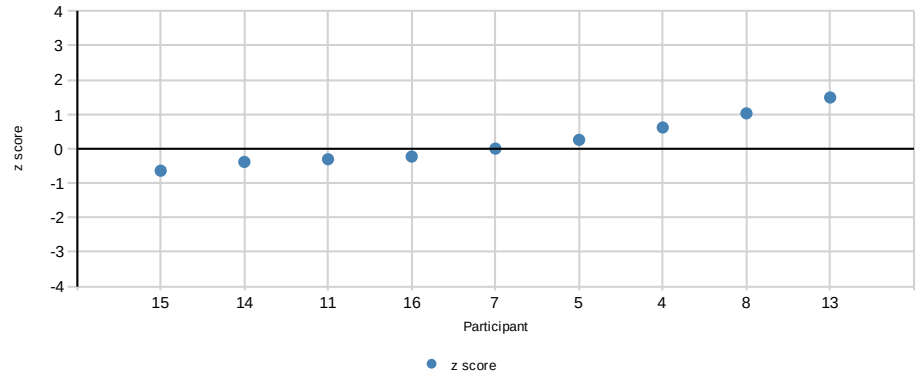
Measurand P_{tot} Sample SO4



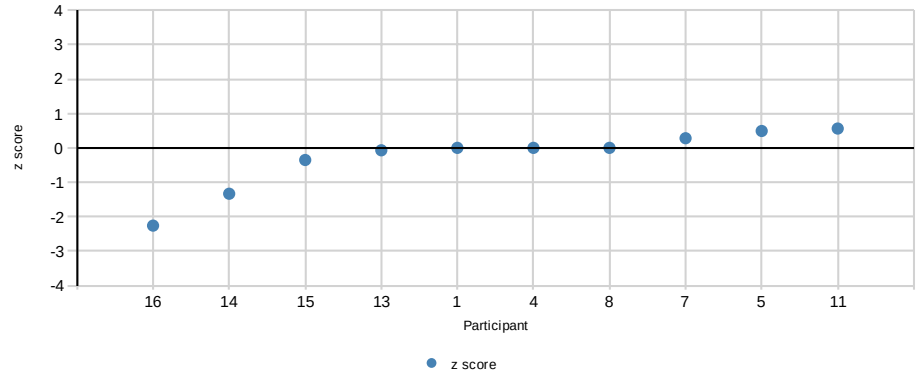
Measurand Se Sample A1M



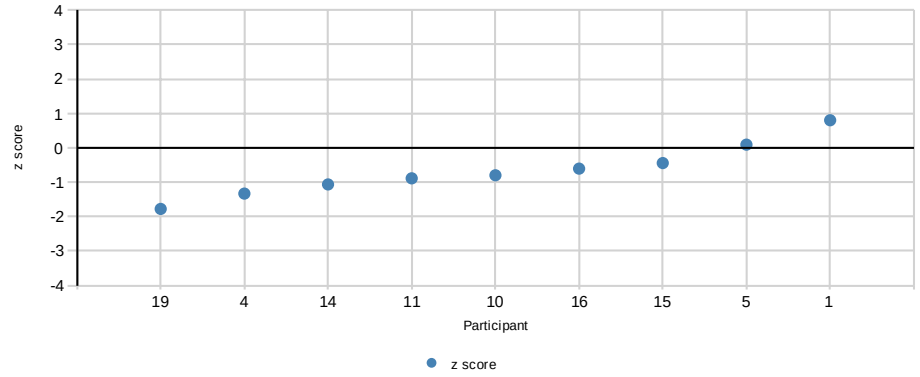
Measurand Se Sample D2M



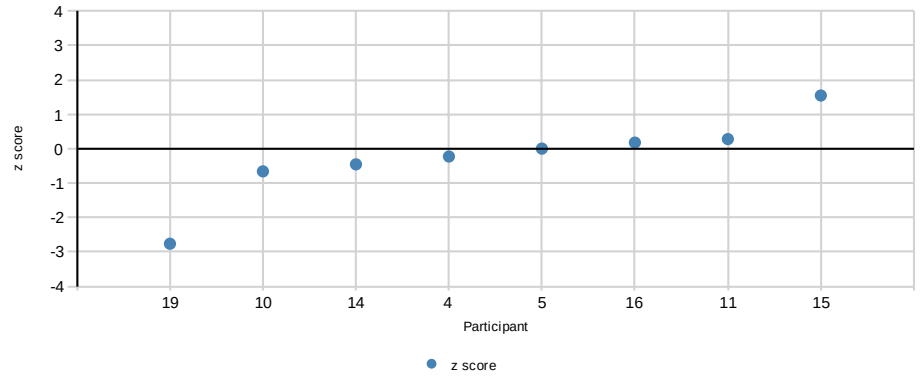
Measurand Se Sample G3M



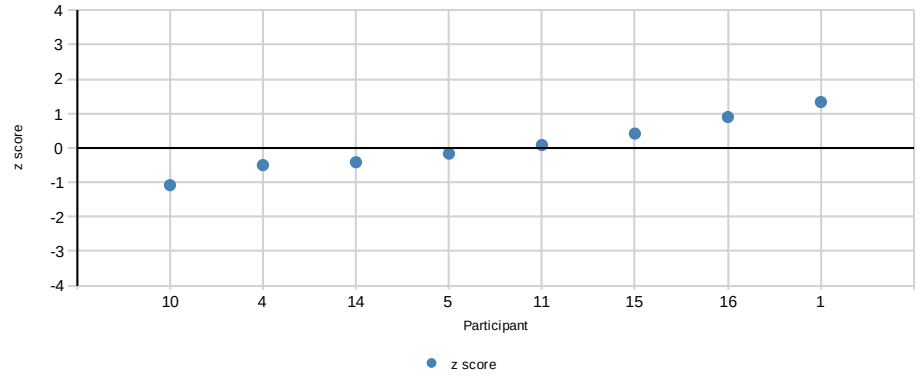
Measurand Ti Sample A1M



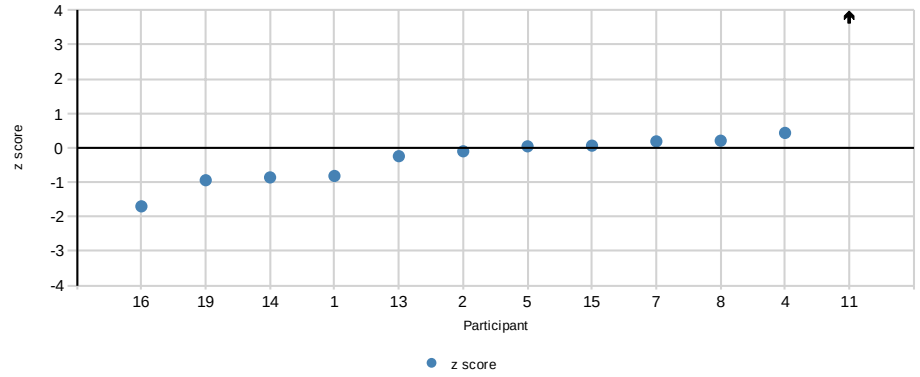
Measurand Ti Sample D2M

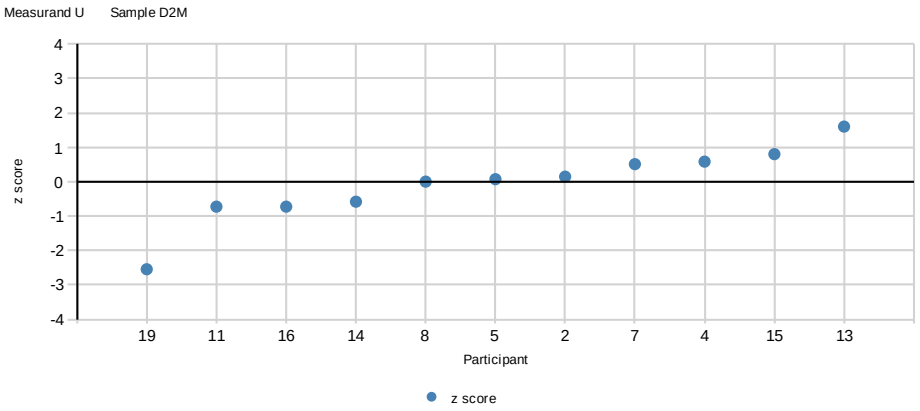


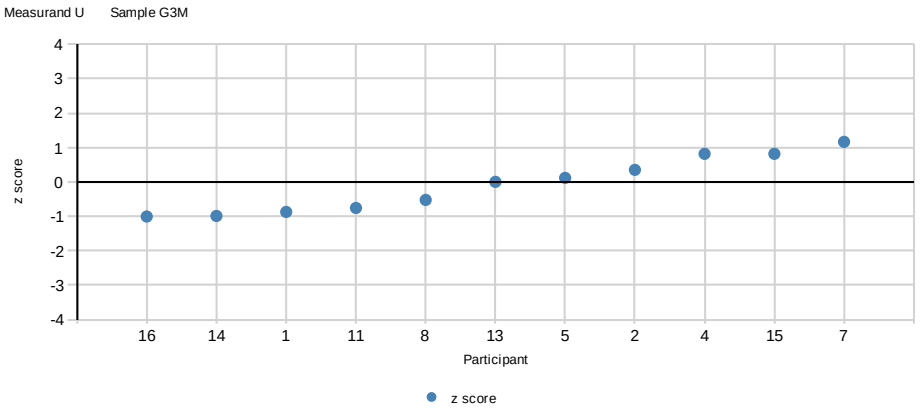
Measurand Ti Sample G3M

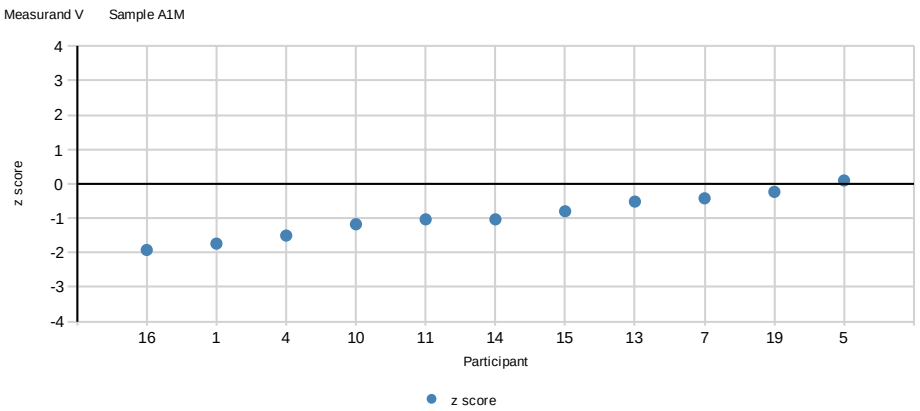


Measurand U Sample A1M

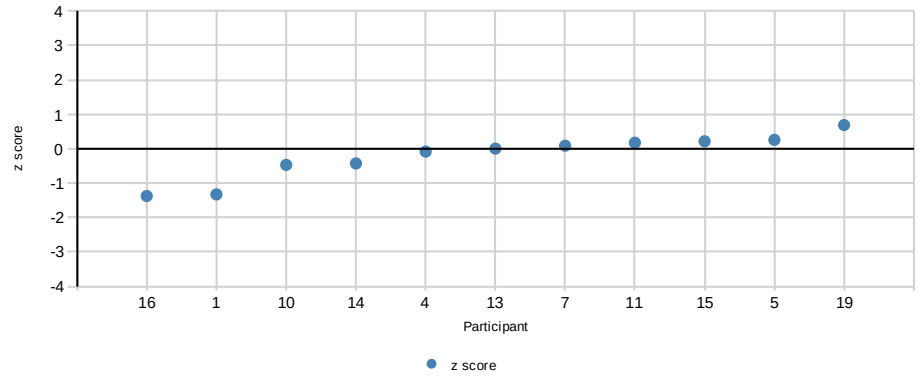



Measurand U Sample D2M
z score
4
3
2
1
0
-1
-2
-3
-4
19 11 16 14 8 5 2 7 4 15 13
Participant
z score

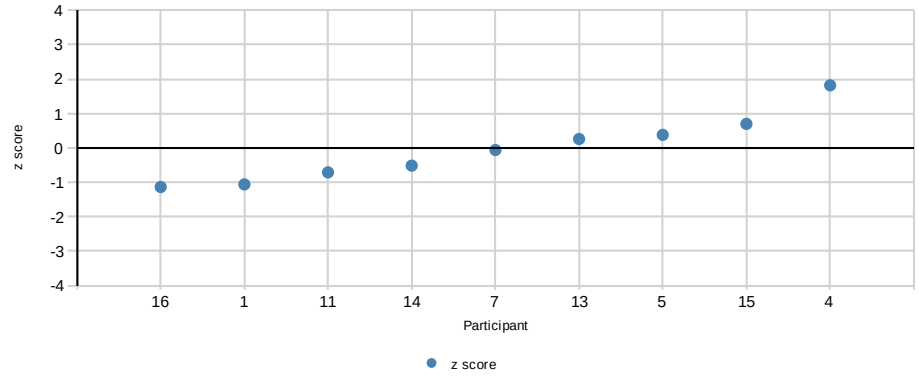

Measurand U Sample G3M
z score
4
3
2
1
0
-1
-2
-3
-4
16 14 1 11 8 13 5 2 4 15 7
Participant
z score


Measurand V Sample A1M
z score
4
3
2
1
0
-1
-2
-3
-4
16 1 4 10 11 14 15 13 7 19 5
Participant
z score

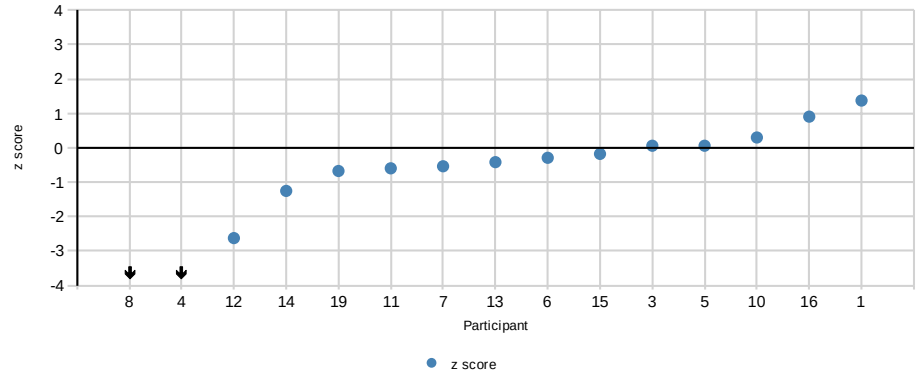
Measurand V Sample D2M

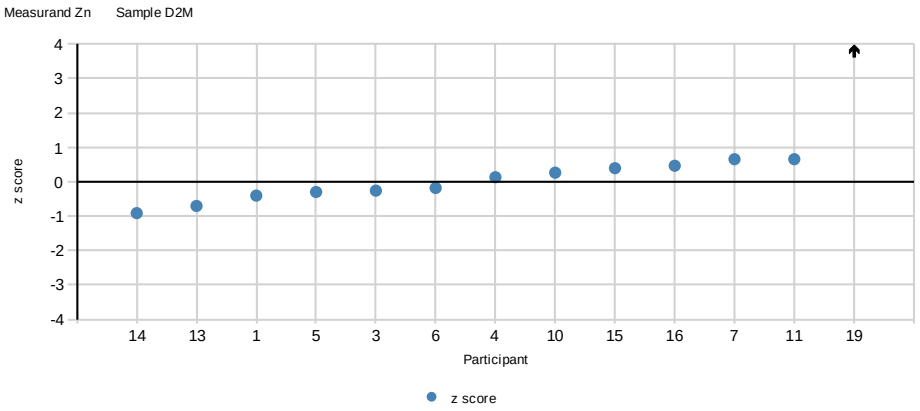


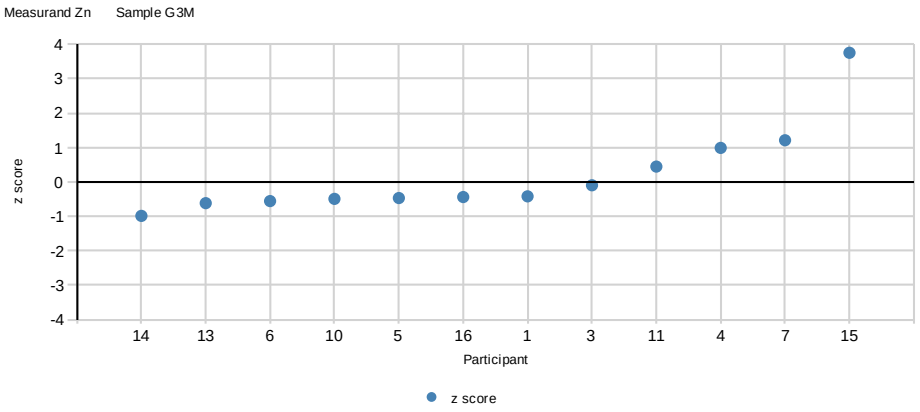
Measurand V Sample G3M

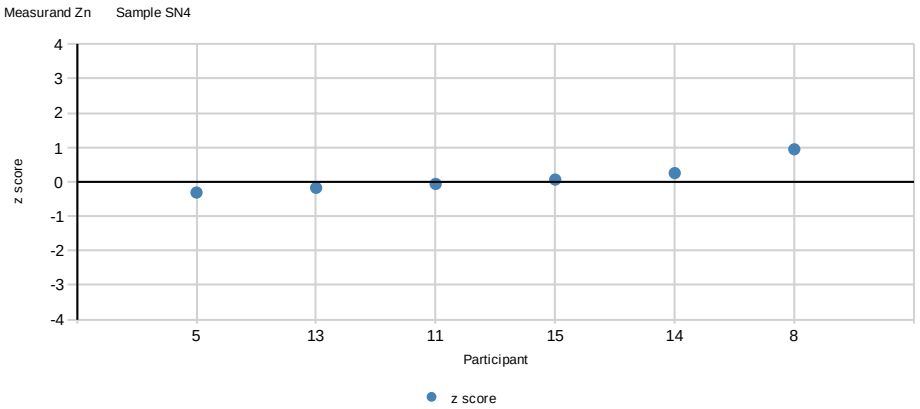


Measurand Zn Sample A1M




Measurand Zn Sample D2M
z score
4
3
2
1
0
-1
-2
-3
-4
14 13 1 5 3 6 4 10 15 16 7 11 19
Participant
z score


Measurand Zn Sample G3M
z score
4
3
2
1
0
-1
-2
-3
-4
14 13 6 10 5 16 1 3 11 4 7 15
Participant
z score

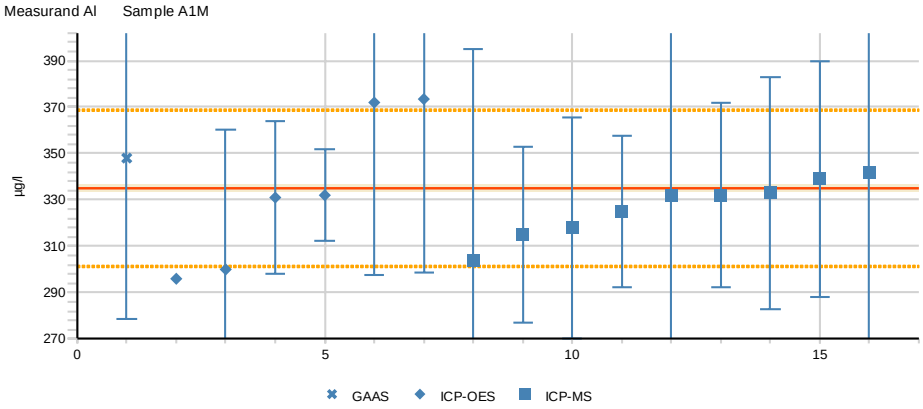

Measurand Zn Sample SN4
z score
4
3
2
1
0
-1
-2
-3
-4
5 13 11 15 14 8
Participant
z score

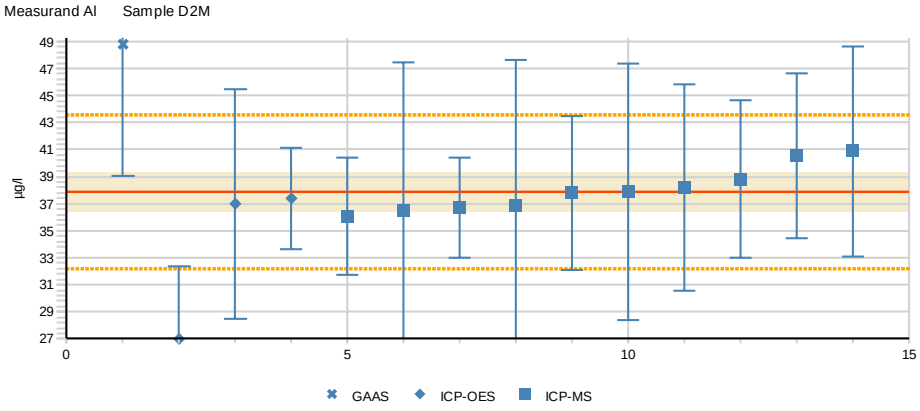
APPENDIX 11: Results grouped according to the methods

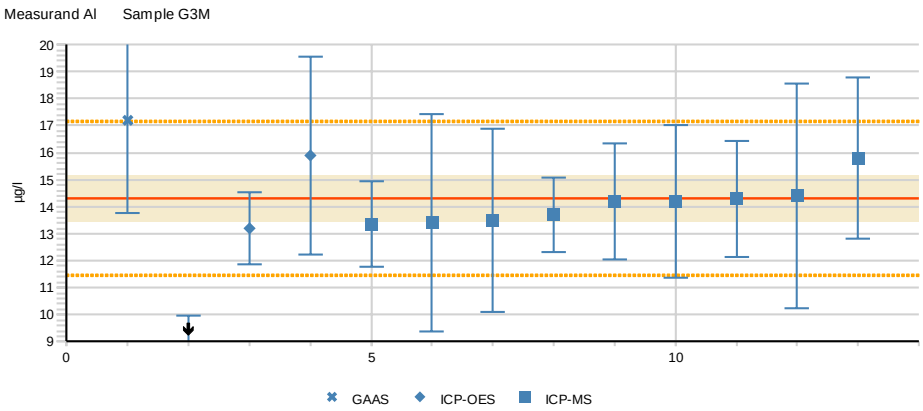
The results are shown in ascending order.

In figures:

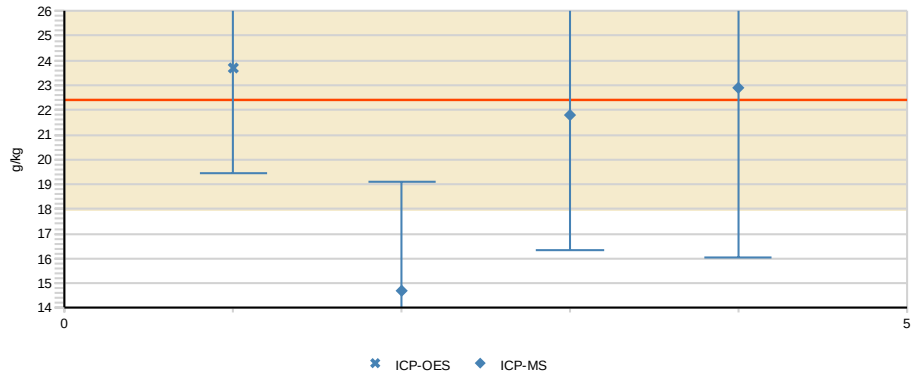
- The dashed lines describe the standard deviation for the proficiency assessment, the red solid line shows the assigned value, the shaded area describes the expanded measurement uncertainty of the assigned value, and the arrow describes the value outside the scale.



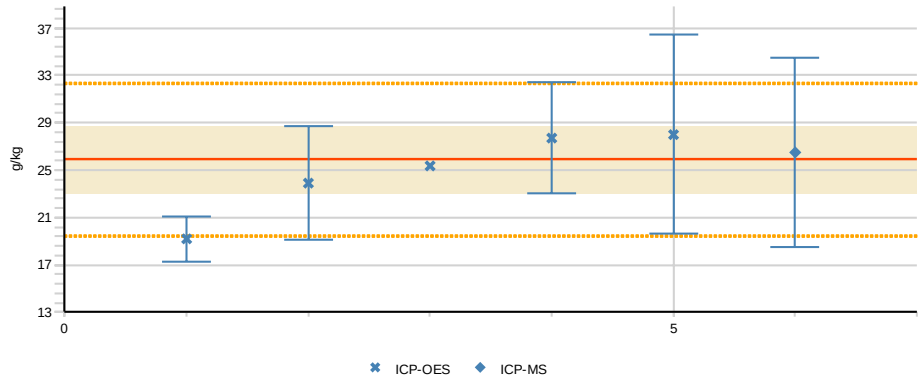




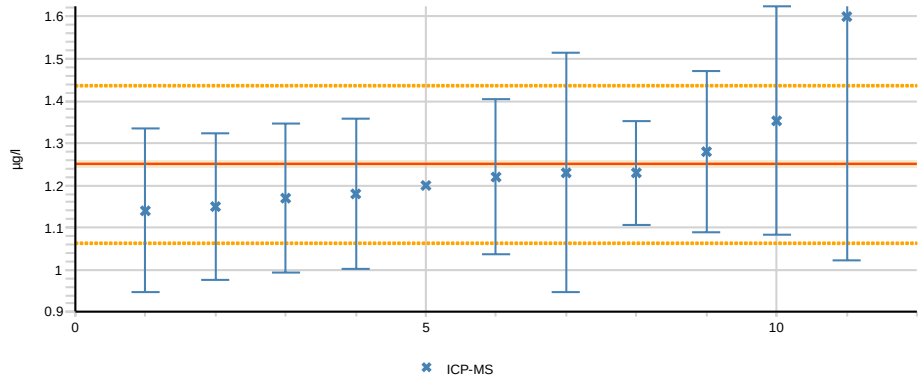
Measurand Al Sample SN4

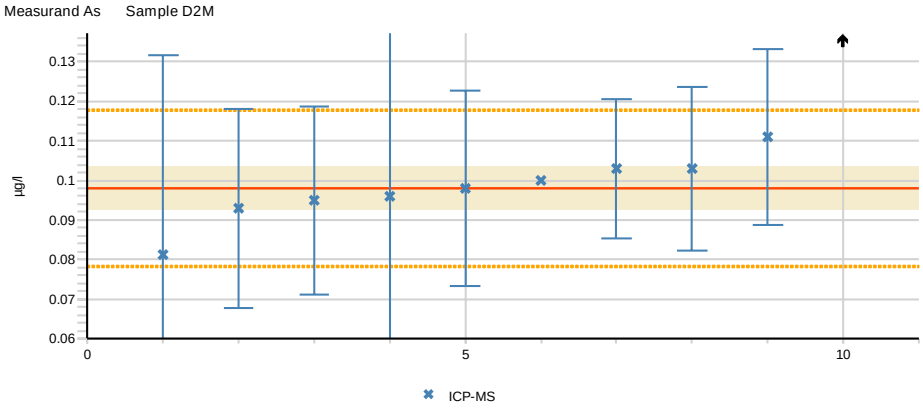


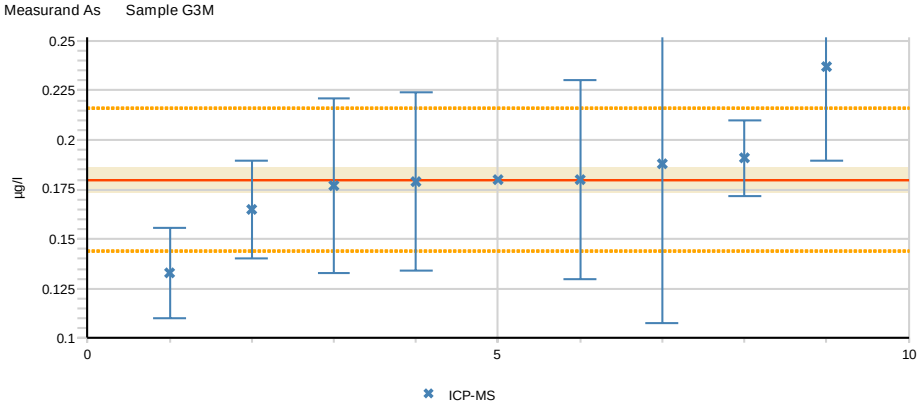
Measurand Al Sample SO4

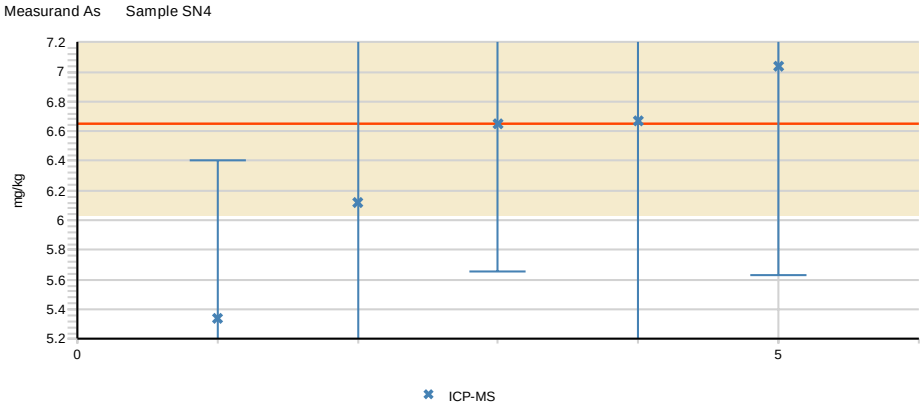


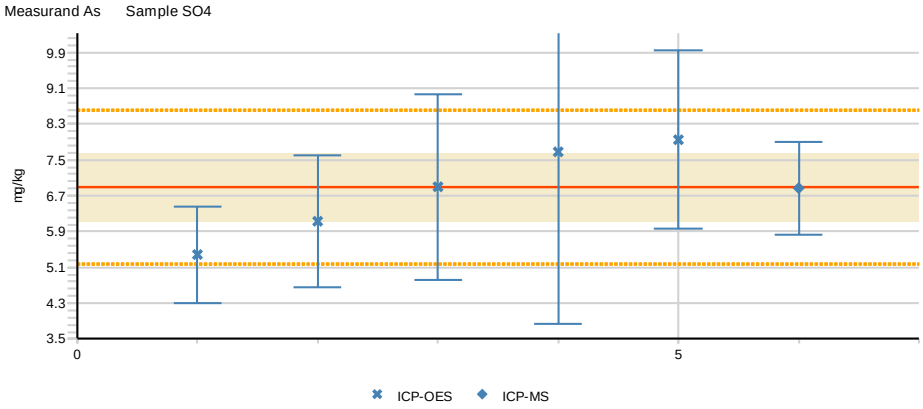
Measurand As Sample A1M

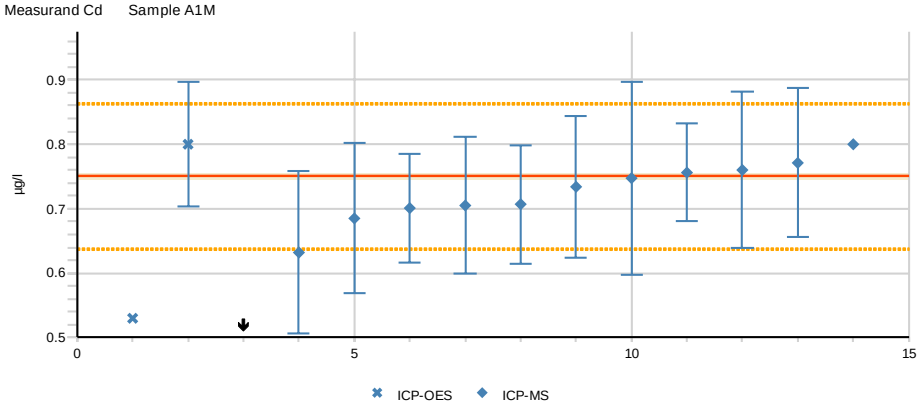


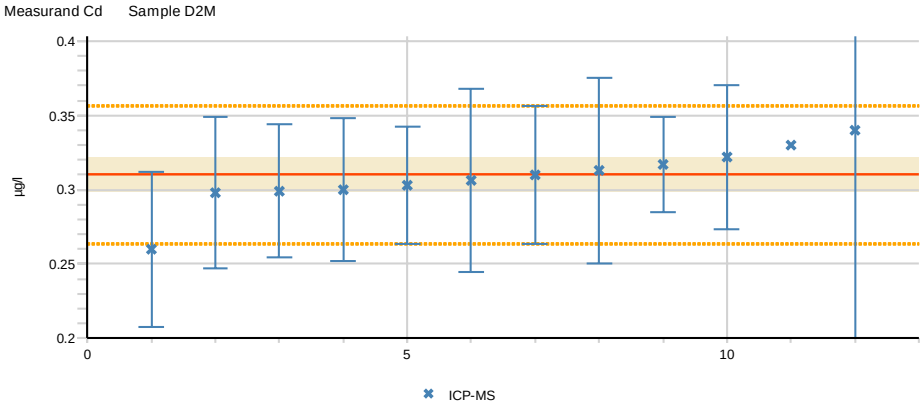

Measurand As
Sample D2M
µg/l
0.13
0.12
0.11
0.1
0.09
0.08
0.07
0.06
0
5
10
ICP-MS

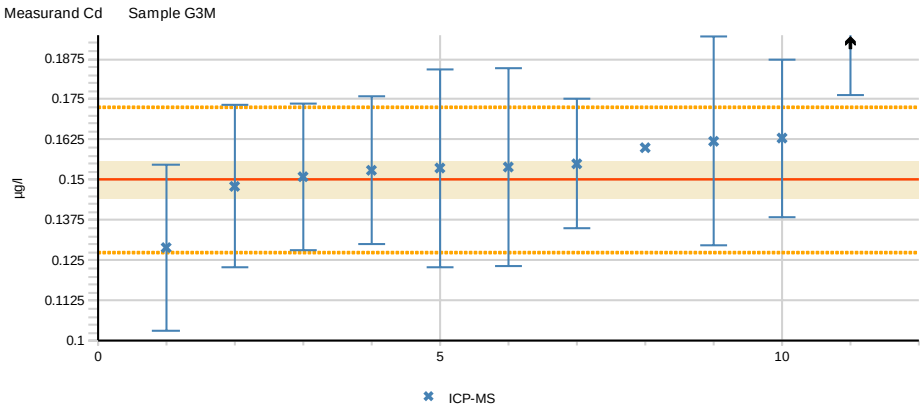

Measurand As
Sample G3M
µg/l
0.25
0.225
0.2
0.175
0.15
0.125
0.1
0
5
10
ICP-MS

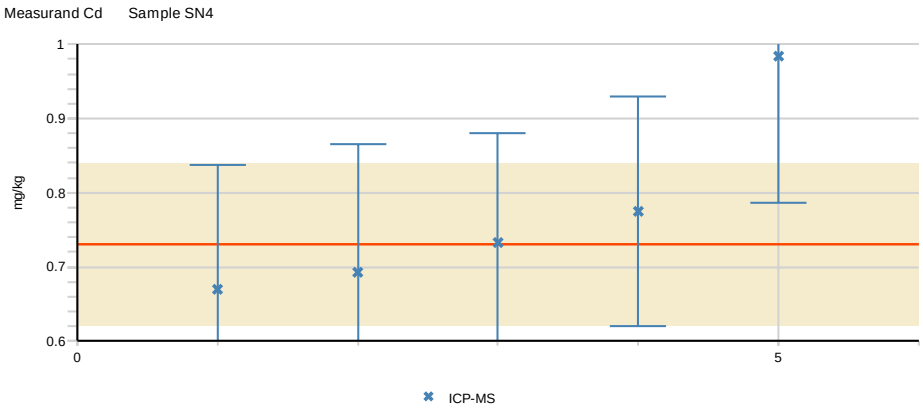

Measurand As
Sample SN4
mg/kg
7.2
7
6.8
6.6
6.4
6.2
6
5.8
5.6
5.4
5.2
0
5
ICP-MS

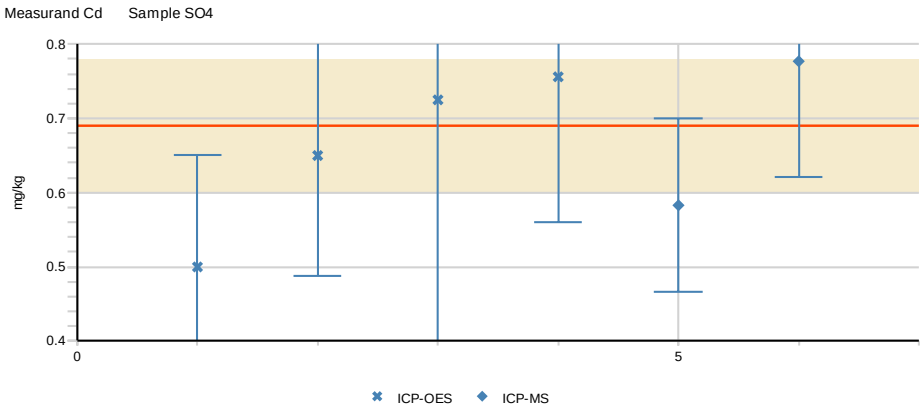

Measurand As
Sample SO4
mg/kg
9.9
9.1
8.3
7.5
6.7
5.9
5.1
4.3
3.5
0
5
ICP-OES
ICP-MS

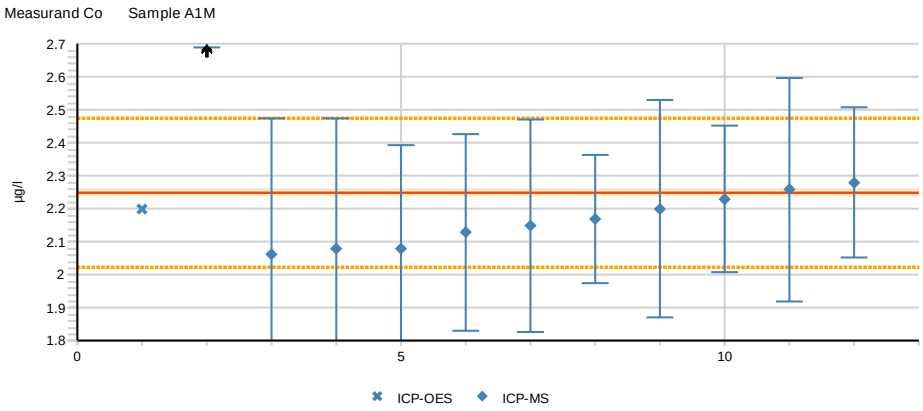

Measurand Cd
Sample A1M
µg/l
0.9
0.8
0.7
0.6
0.5
0
5
10
15
ICP-OES
ICP-MS

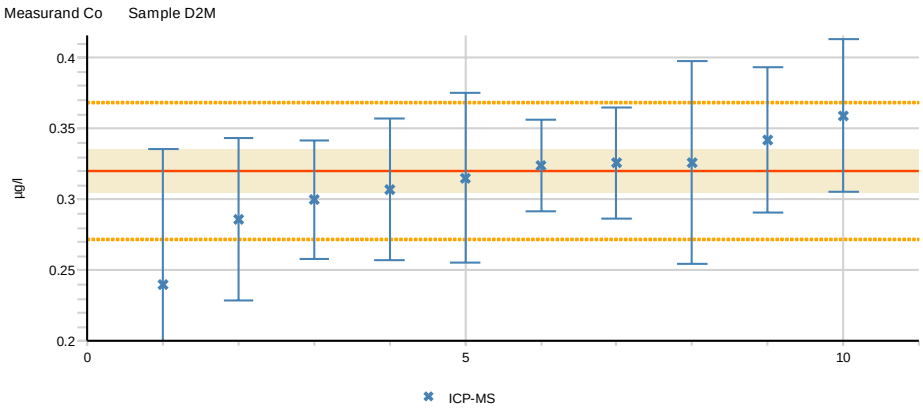

Measurand Cd
Sample D2M
µg/l
0.4
0.35
0.3
0.25
0.2
0
5
10
ICP-MS

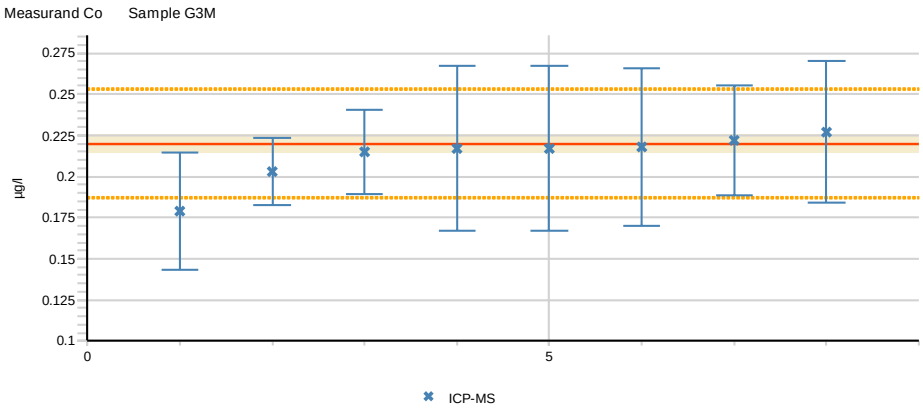

Measurand Cd
Sample G3M
µg/l
0.1875
0.175
0.1625
0.15
0.1375
0.125
0.1125
0.1
0
5
10
ICP-MS


Measurand Cd
Sample SN4
mg/kg
1
0.9
0.8
0.7
0.6
0
5
ICP-MS

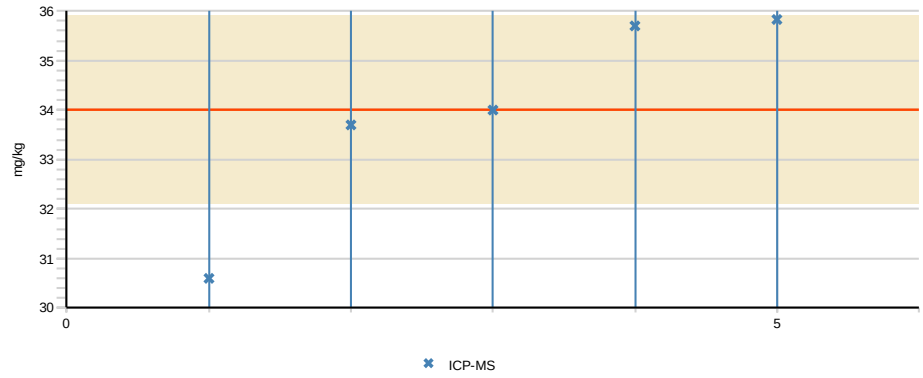

Measurand Cd
Sample SO4
mg/kg
0.8
0.7
0.6
0.5
0.4
0
5
ICP-OES
ICP-MS


Measurand Co
Sample A1M
µg/l
2.7
2.6
2.5
2.4
2.3
2.2
2.1
2
1.9
1.8
0
5
10
ICP-OES
ICP-MS

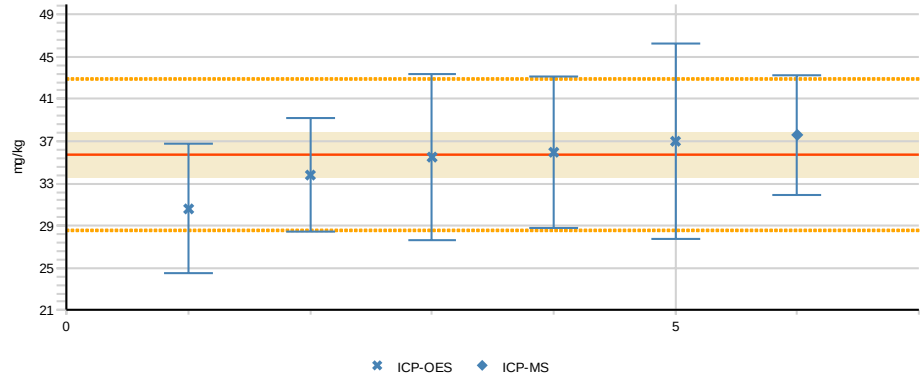

Measurand Co
Sample D2M
µg/l
0.4
0.35
0.3
0.25
0.2
0
5
10
ICP-MS


Measurand Co
Sample G3M
µg/l
0.275
0.25
0.225
0.2
0.175
0.15
0.125
0.1
0
5
ICP-MS

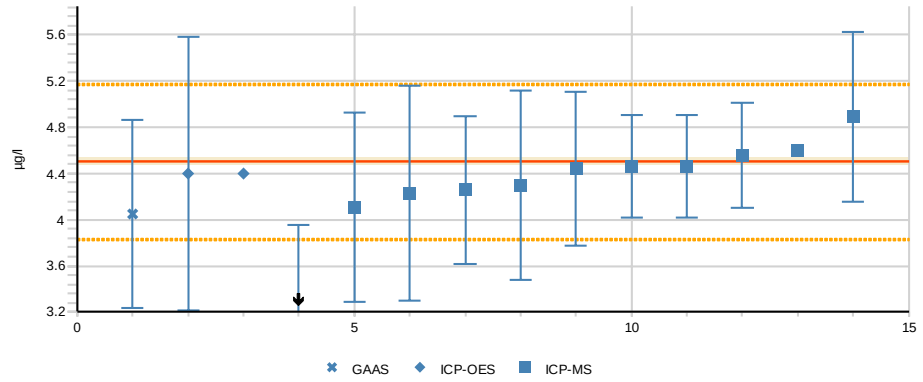
Measurand Co Sample SN4

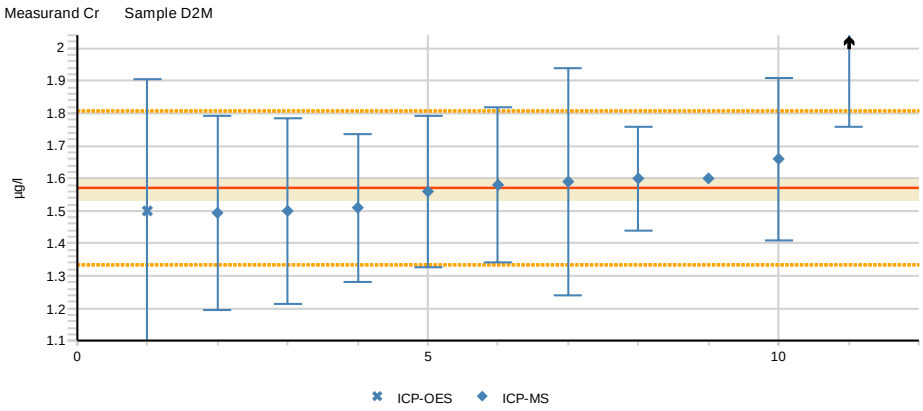


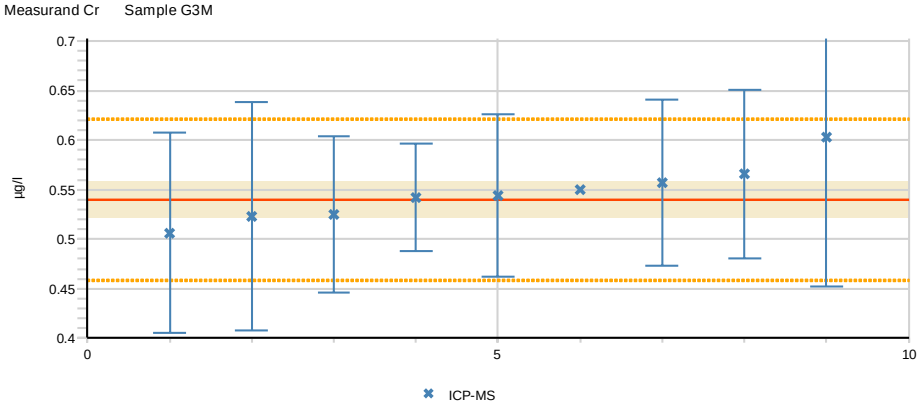
Measurand Co Sample SO4

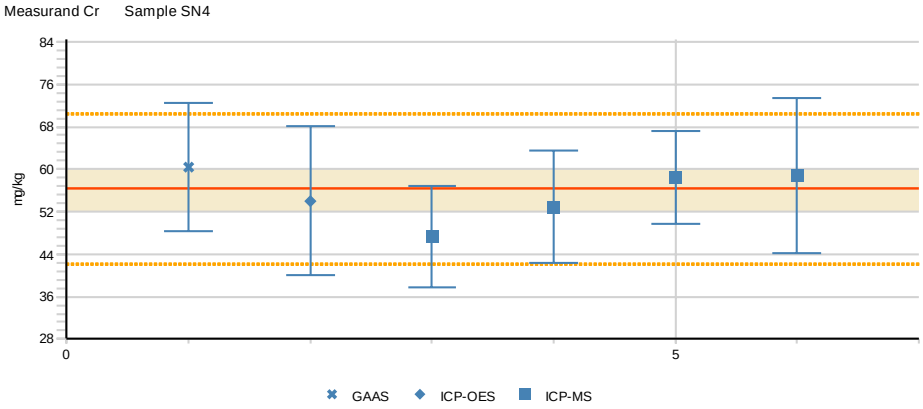


Measurand Cr Sample A1M

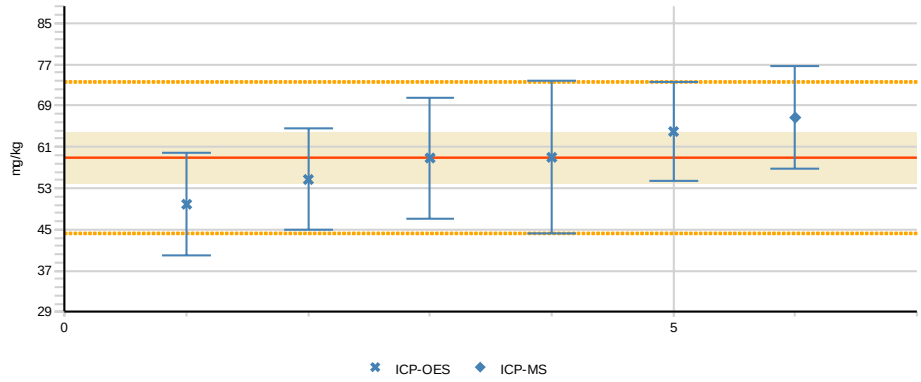



Measurand Cr Sample D2M
µg/l
2
1.9
1.8
1.7
1.6
1.5
1.4
1.3
1.2
1.1
0
5
10
ICP-OES
ICP-MS

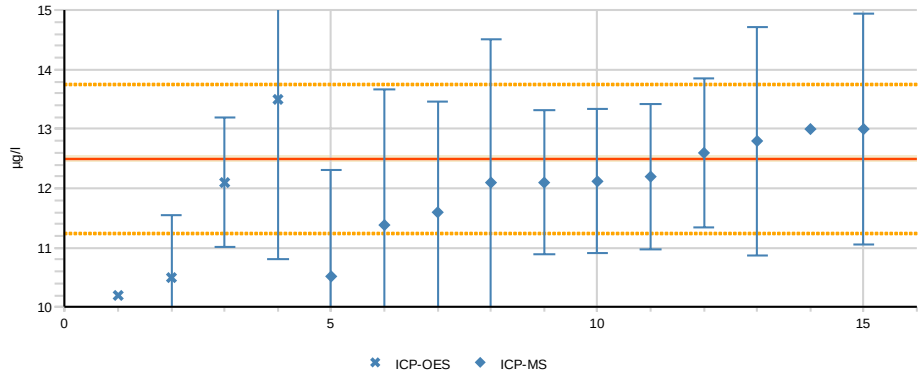

Measurand Cr Sample G3M
µg/l
0.7
0.65
0.6
0.55
0.5
0.45
0.4
0
5
10
ICP-MS


Measurand Cr Sample SN4
mg/kg
84
76
68
60
52
44
36
28
0
5
GAAS
ICP-OES
ICP-MS

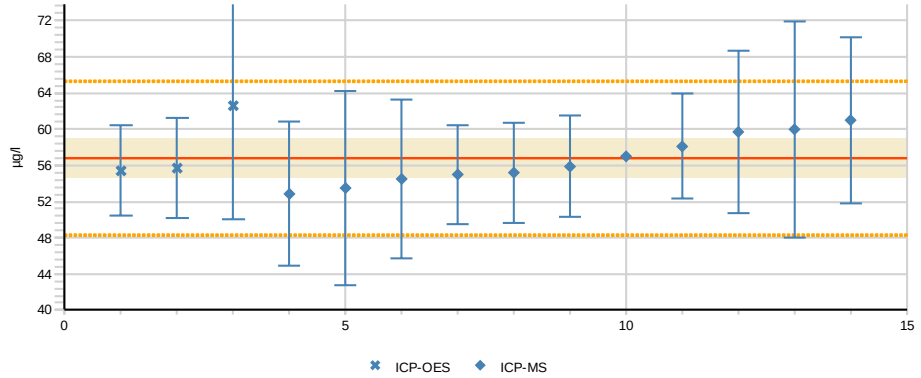
Measurand Cr Sample SO4

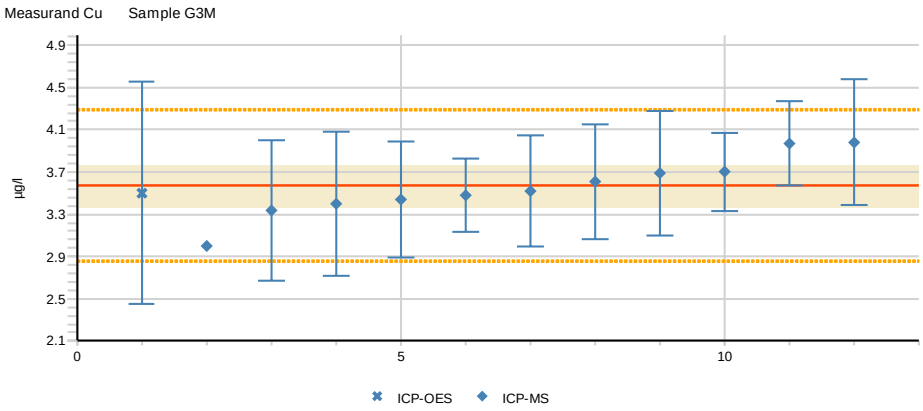


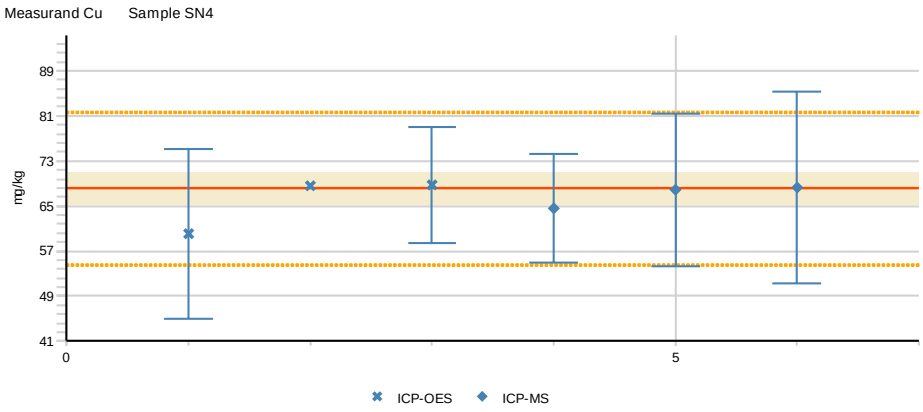
Measurand Cu Sample A1M

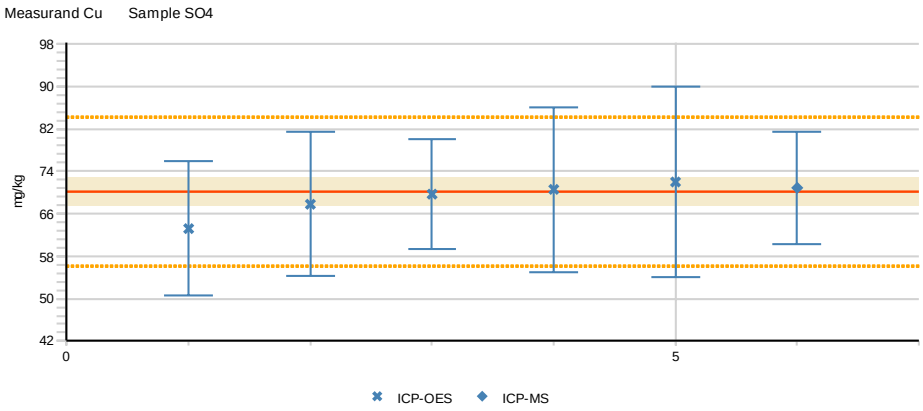


Measurand Cu Sample D2M

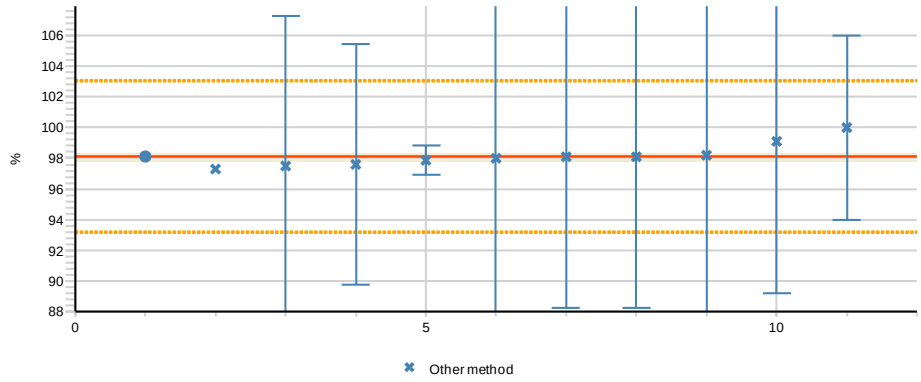



Measurand Cu Sample G3M
µg/l
4.9
4.5
4.1
3.7
3.3
2.9
2.5
2.1
0
5
10
ICP-OES
ICP-MS

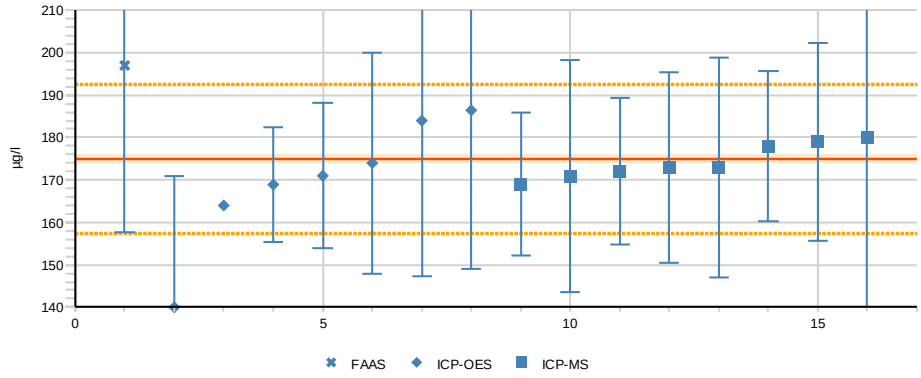

Measurand Cu Sample SN4
mg/kg
89
81
73
65
57
49
41
0
5
ICP-OES
ICP-MS


Measurand Cu Sample SO4
mg/kg
98
90
82
74
66
58
50
42
0
5
ICP-OES
ICP-MS

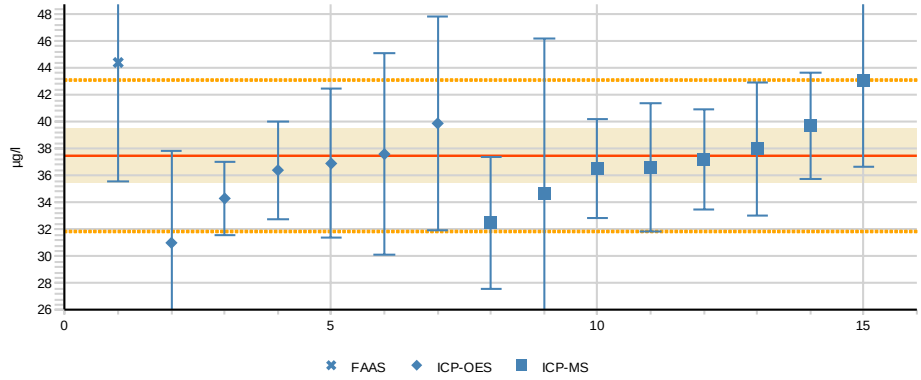
Measurand Drw Sample S4M

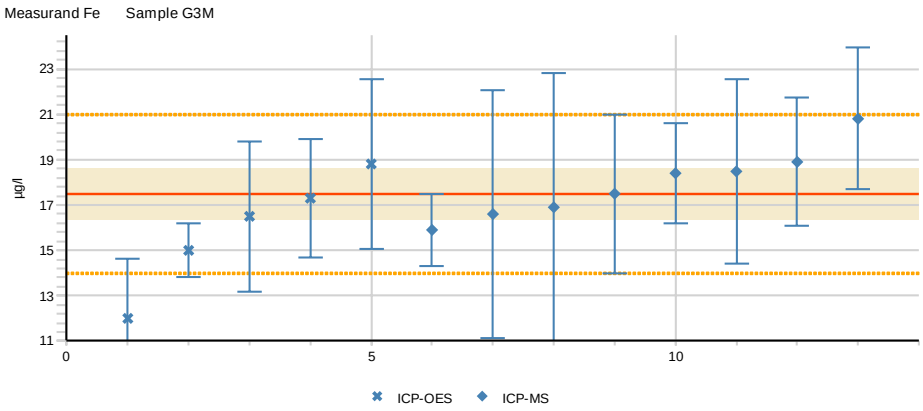


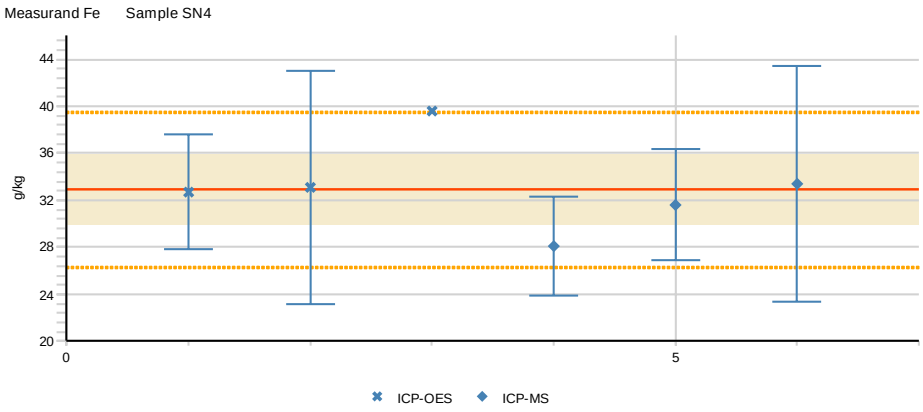
Measurand Fe Sample A1M

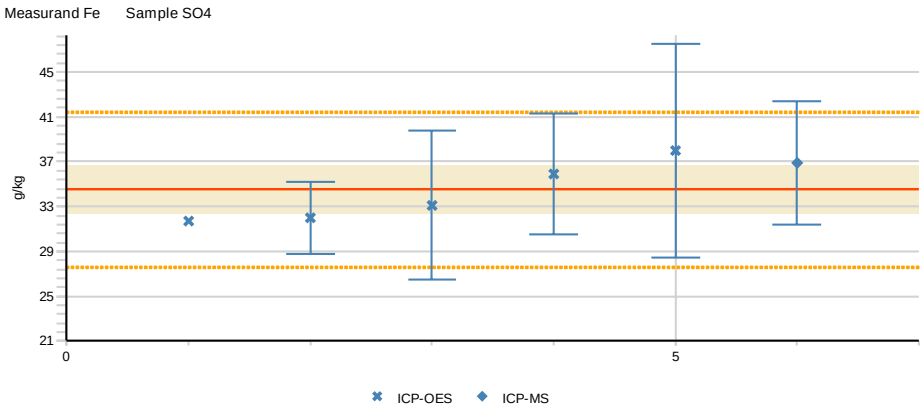


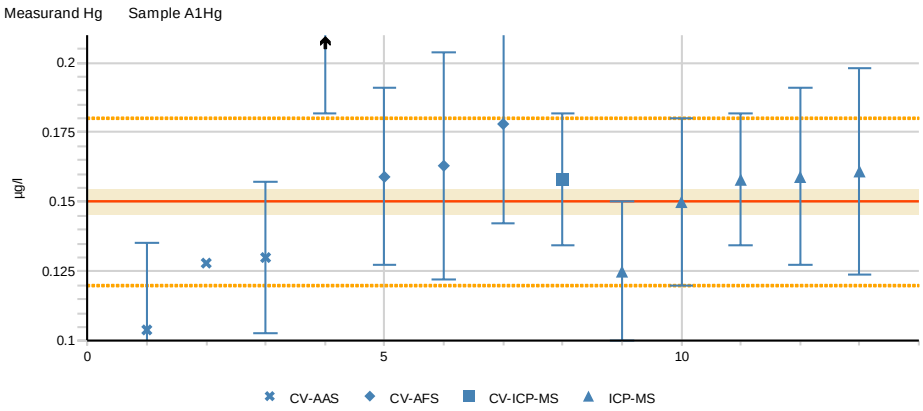
Measurand Fe Sample D2M

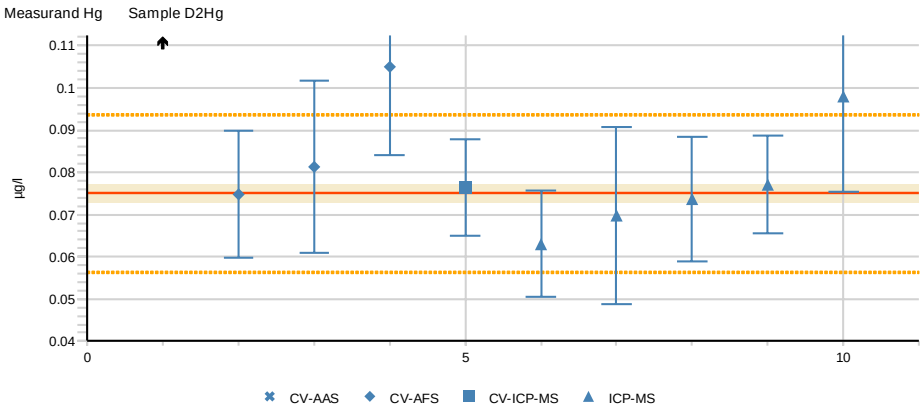


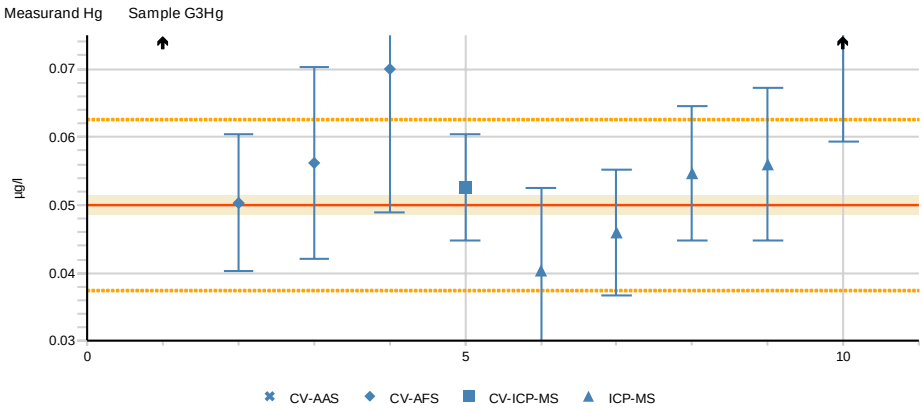

Measurand Fe Sample G3M
µg/l
23
21
19
17
15
13
11
0
5
10
ICP-OES
ICP-MS

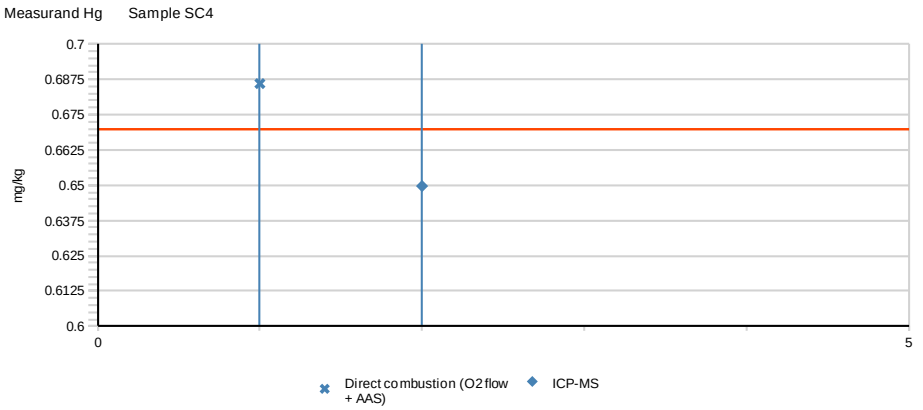

Measurand Fe Sample SN4
g/kg
44
40
36
32
28
24
20
0
5
ICP-OES
ICP-MS

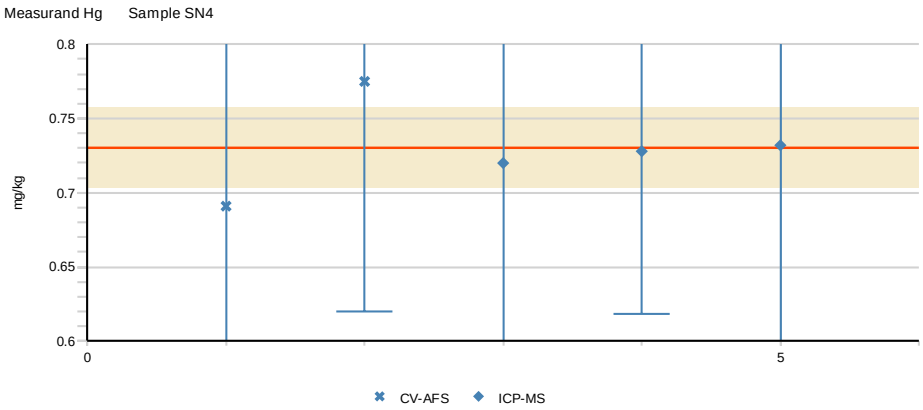

Measurand Fe Sample SO4
g/kg
45
41
37
33
29
25
21
0
5
ICP-OES
ICP-MS

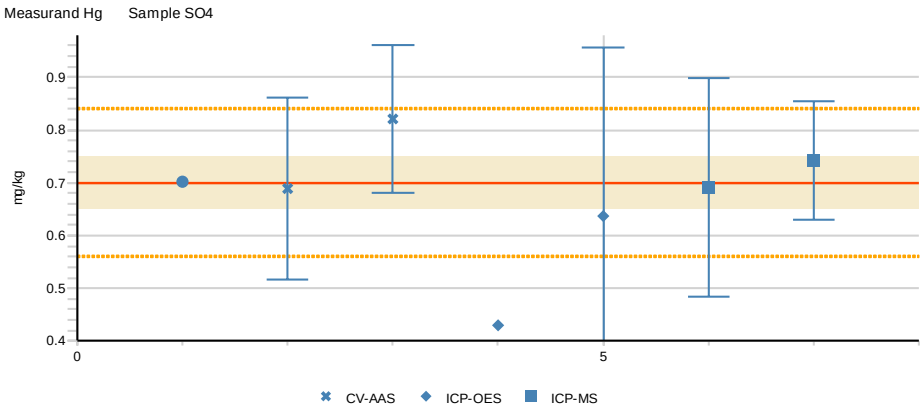

Measurand Hg
Sample A1Hg
µg/l
0.2
0.175
0.15
0.125
0.1
0
5
10
CV-AAS
CV-AFS
CV-ICP-MS
ICP-MS


Measurand Hg
Sample D2Hg
µg/l
0.11
0.1
0.09
0.08
0.07
0.06
0.05
0.04
0
5
10
CV-AAS
CV-AFS
CV-ICP-MS
ICP-MS

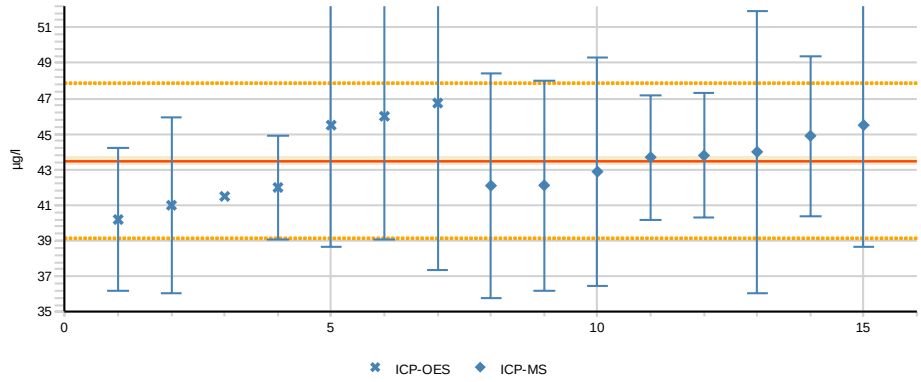

Measurand Hg
Sample G3Hg
µg/l
0.07
0.06
0.05
0.04
0.03
0
5
10
CV-AAS
CV-AFS
CV-ICP-MS
ICP-MS


Measurand Hg
Sample SC4
0.7
0.6875
0.675
0.6625
0.65
0.6375
0.625
0.6125
0.6
mg/kg
0
5
Direct combustion (O2 flow + AAS)
ICP-MS

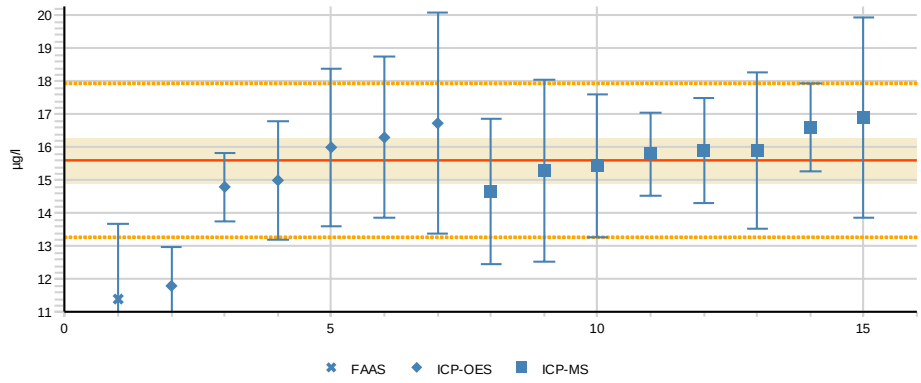

Measurand Hg
Sample SN4
0.8
0.75
0.7
0.65
0.6
mg/kg
0
5
CV-AFS
ICP-MS


Measurand Hg
Sample SO4
0.9
0.8
0.7
0.6
0.5
0.4
mg/kg
0
5
CV-AAS
ICP-OES
ICP-MS

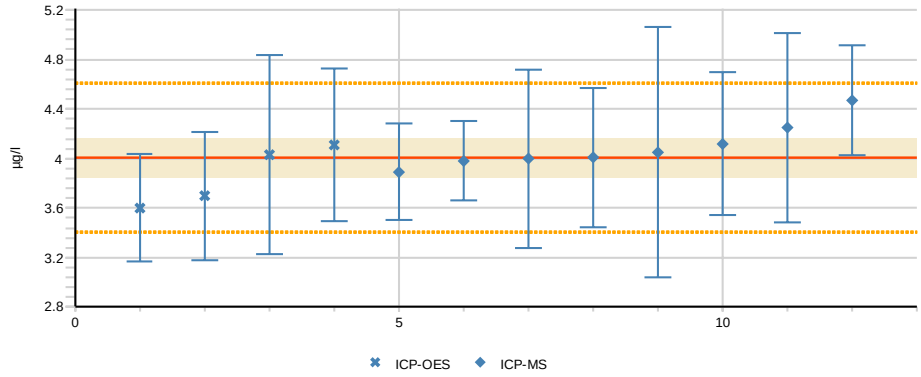
Measurand Mn Sample A1M

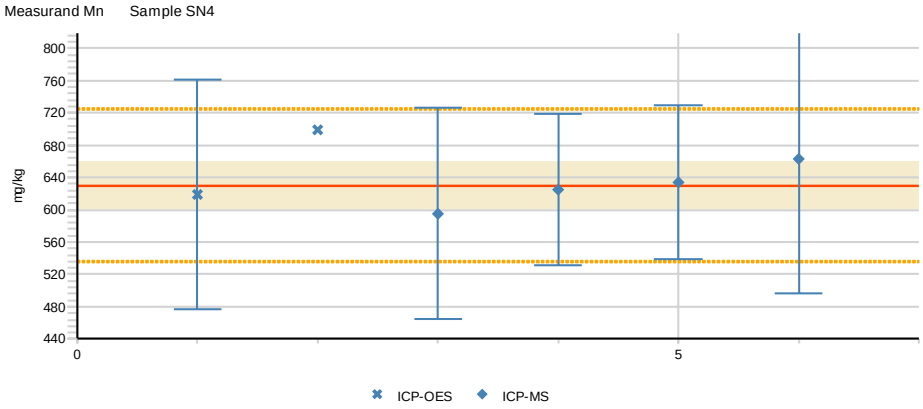


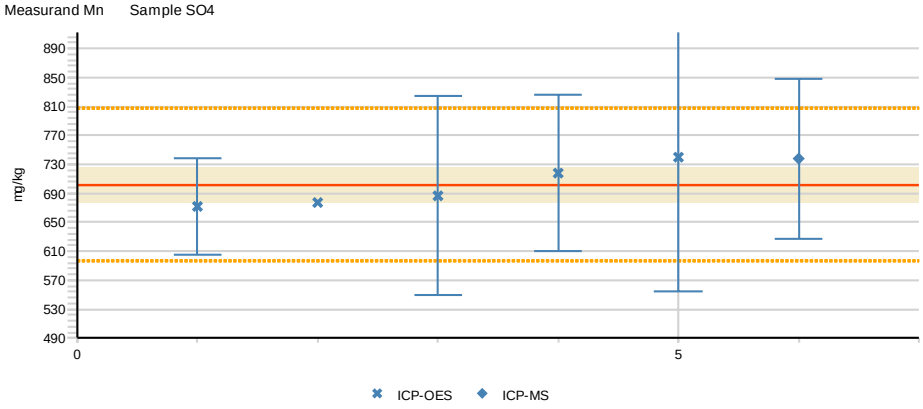
Measurand Mn Sample D2M

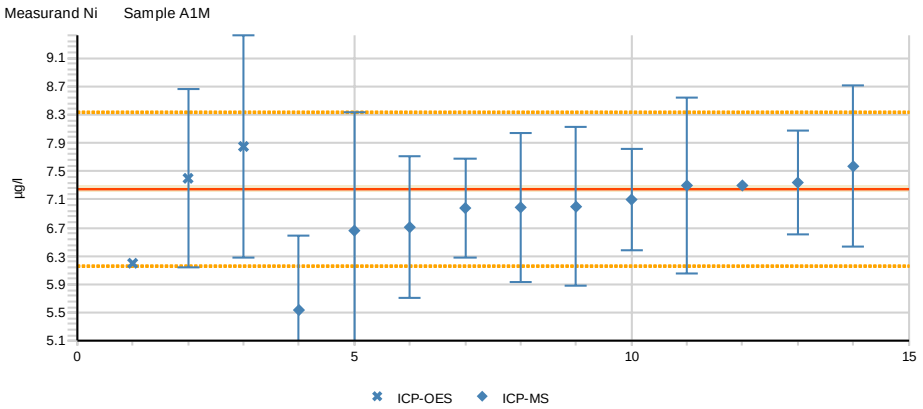


Measurand Mn Sample G3M

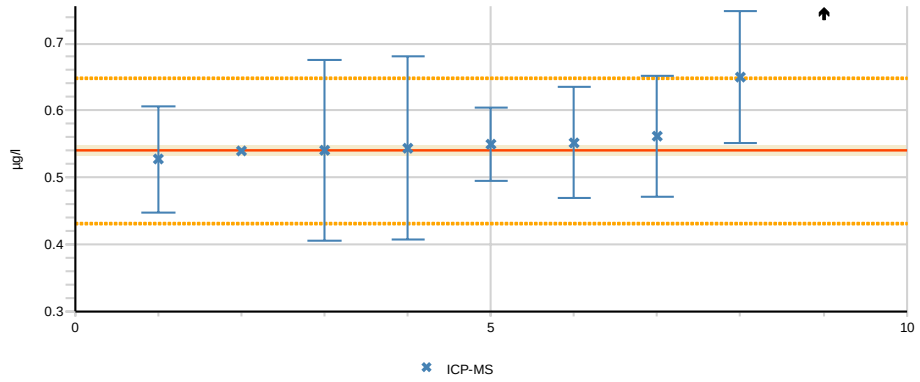



Measurand Mn Sample SN4
mg/kg
800
760
720
680
640
600
560
520
480
440
0
5
ICP-OES
ICP-MS

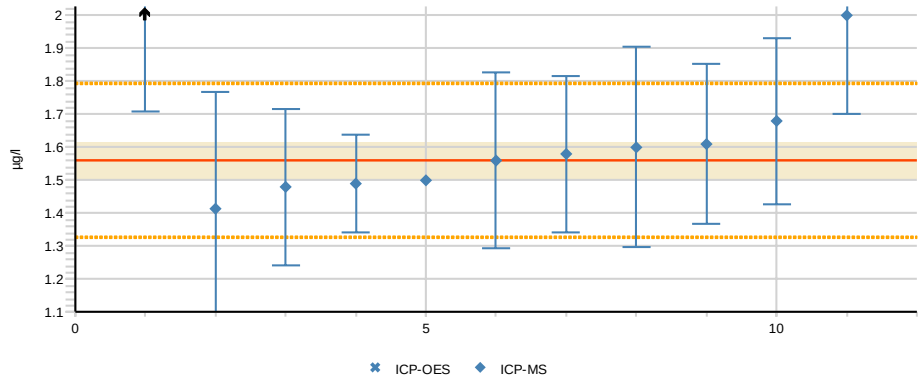

Measurand Mn Sample SO4
mg/kg
890
850
810
770
730
690
650
610
570
530
490
0
5
ICP-OES
ICP-MS


Measurand Ni Sample A1M
µg/l
9.1
8.7
8.3
7.9
7.5
7.1
6.7
6.3
5.9
5.5
5.1
0
5
10
15
ICP-OES
ICP-MS

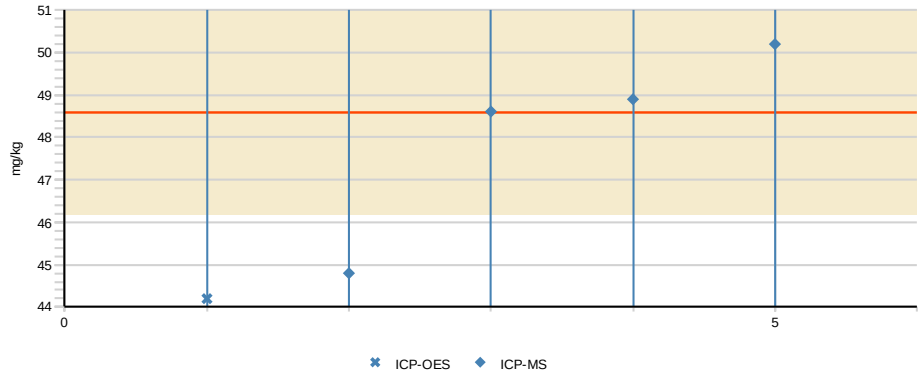
Measurand Ni Sample D2M



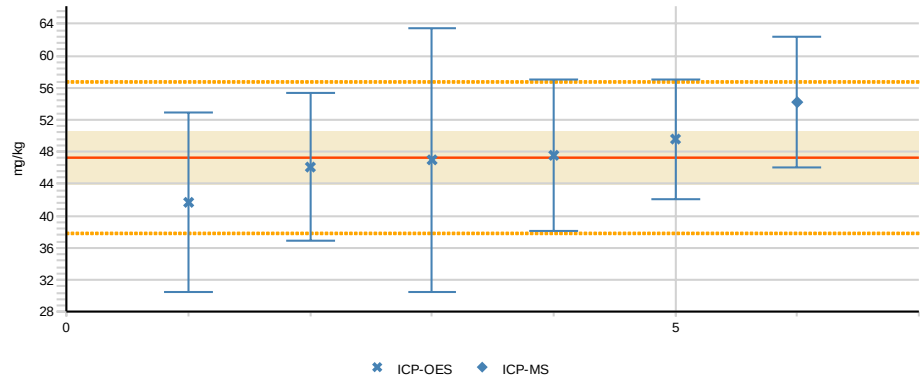
Measurand Ni Sample G3M



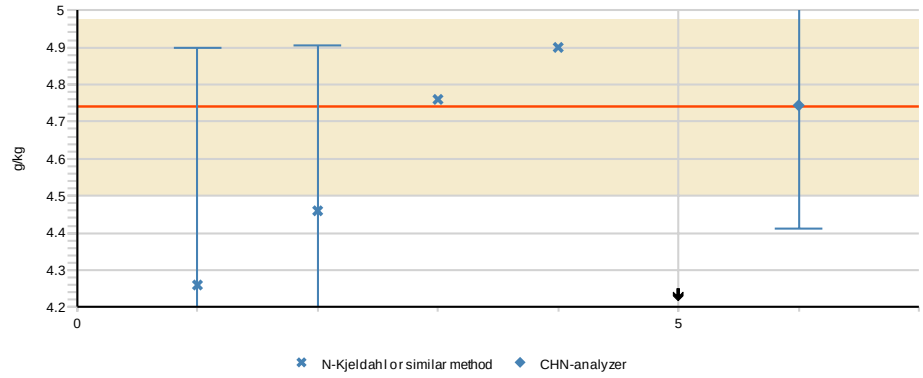
Measurand Ni Sample SN4



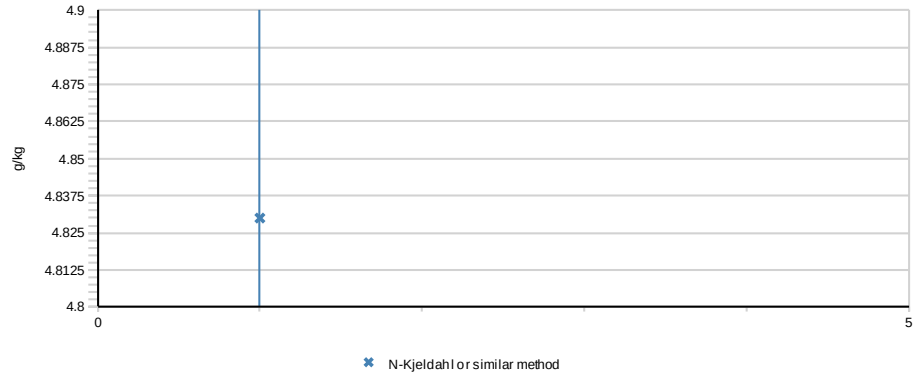
Measurand Ni Sample SO4

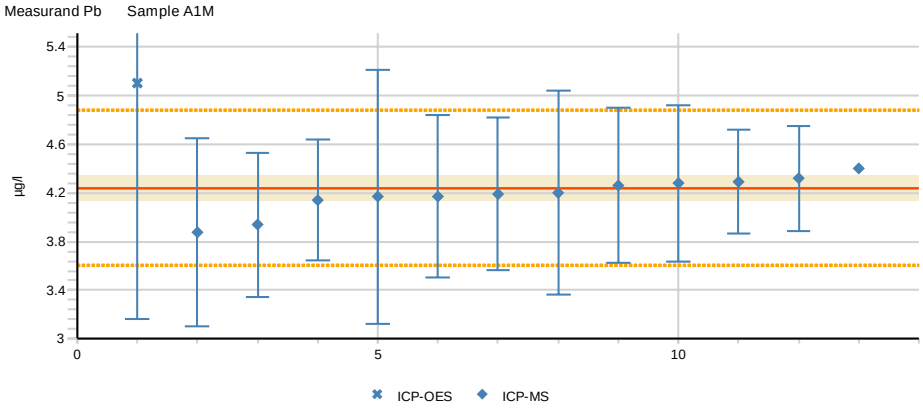


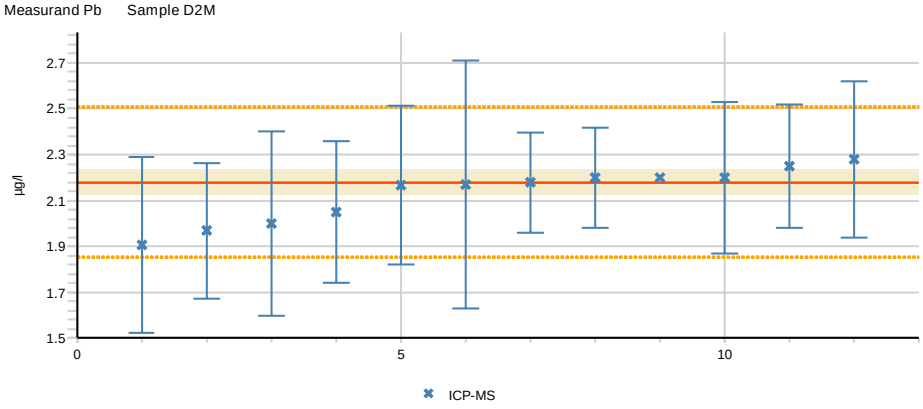
Measurand N_{tot} Sample SN4

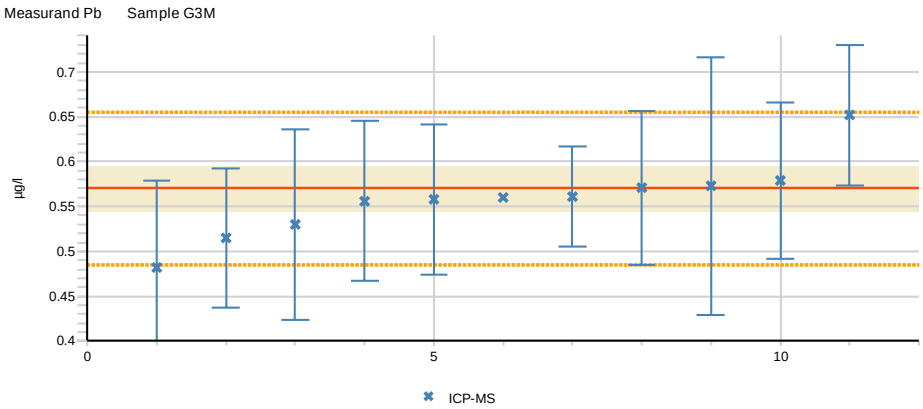


Measurand N_{tot} Sample SO4

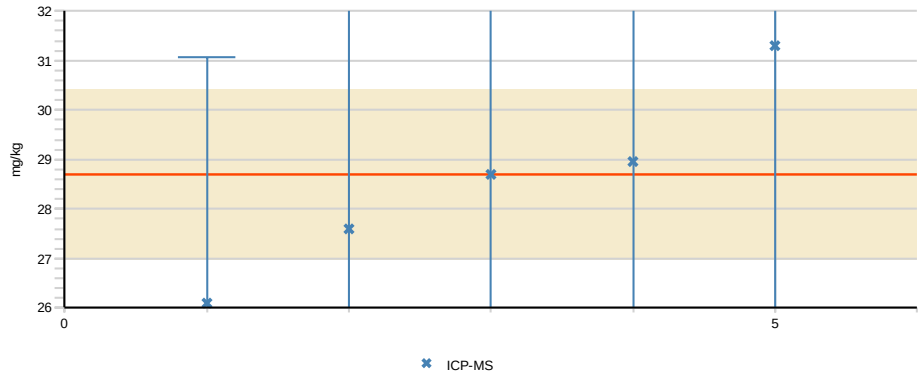



Measurand Pb
Sample A1M
µg/l
5.4
5
4.6
4.2
3.8
3.4
3
0
5
10
ICP-OES
ICP-MS

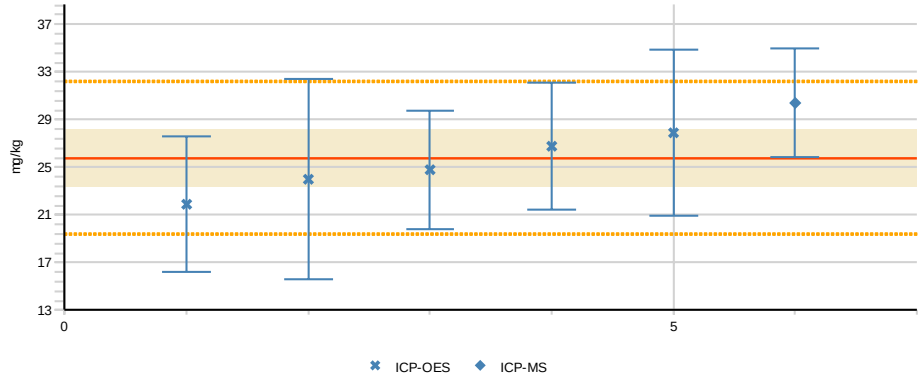

Measurand Pb
Sample D2M
µg/l
2.7
2.5
2.3
2.1
1.9
1.7
1.5
0
5
10
ICP-MS


Measurand Pb
Sample G3M
µg/l
0.7
0.65
0.6
0.55
0.5
0.45
0.4
0
5
10
ICP-MS

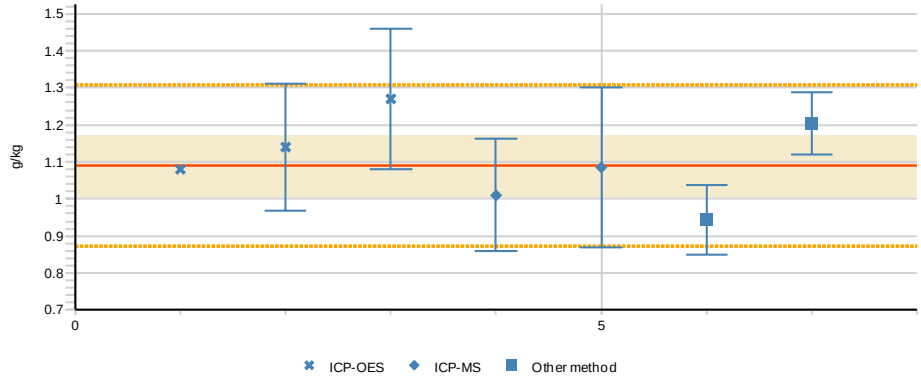
Measurand Pb Sample SN4



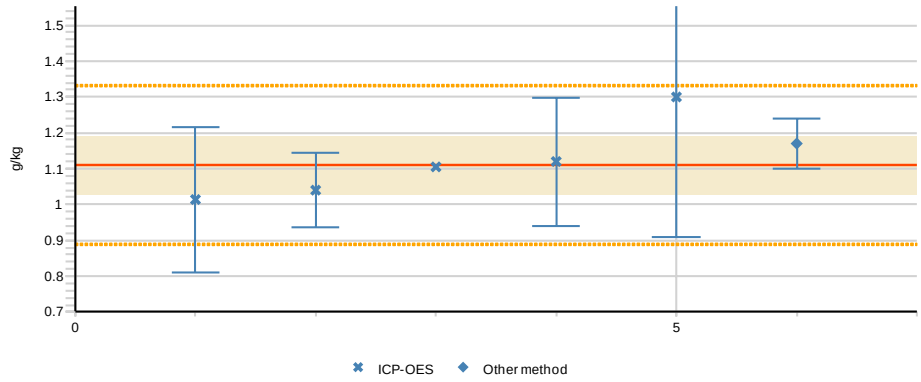
Measurand Pb Sample SO4



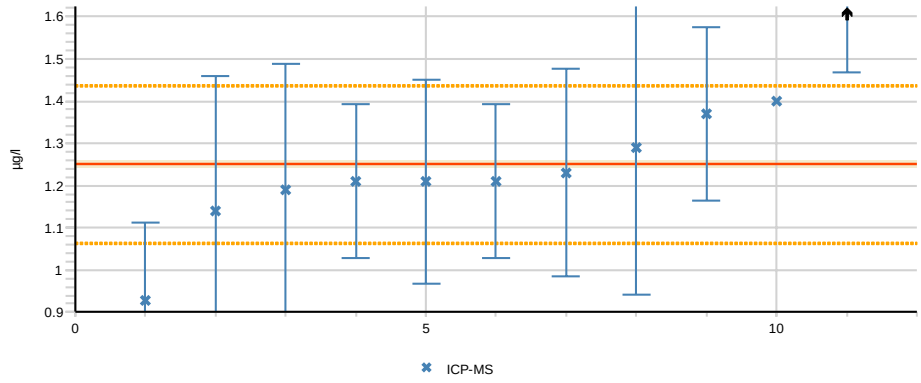
Measurand P_{tot} Sample SN4



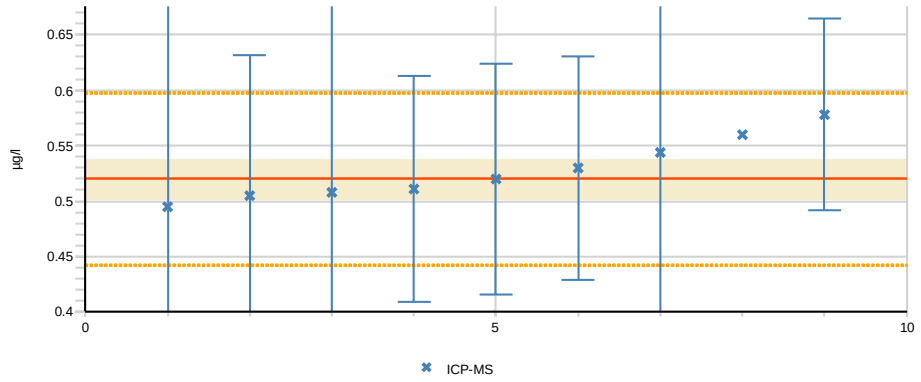
Measurand P_{tot} Sample SO4

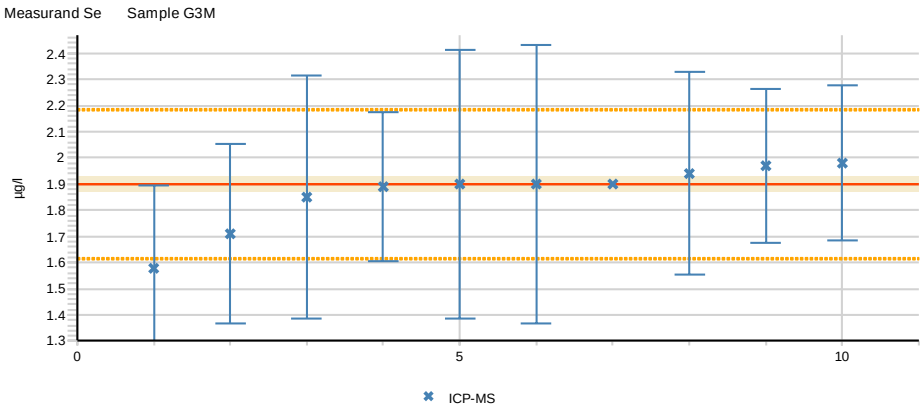


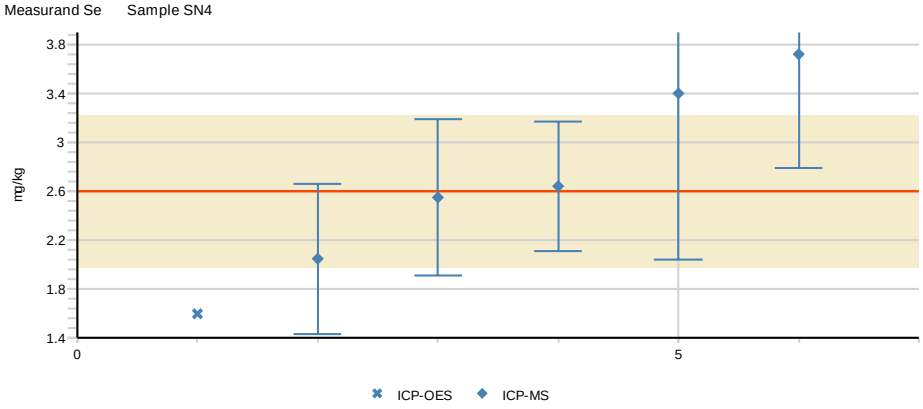
Measurand Se Sample A1M

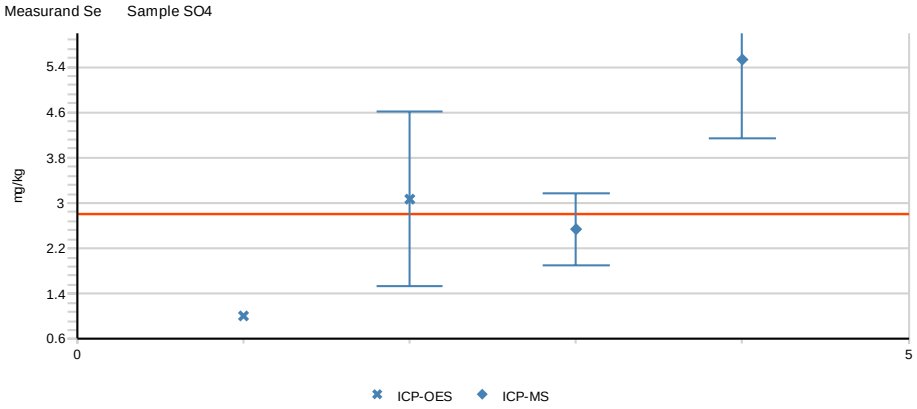


Measurand Se Sample D2M

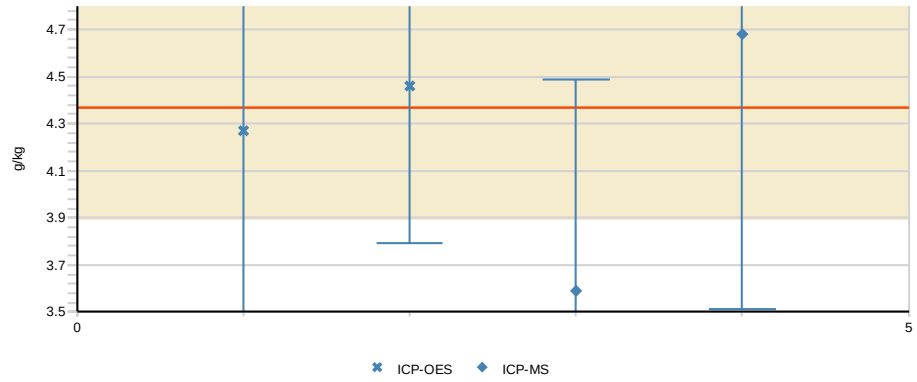



Measurand Se
Sample G3M
µg/l
2.4
2.3
2.2
2.1
2
1.9
1.8
1.7
1.6
1.5
1.4
1.3
0
5
10
ICP-MS

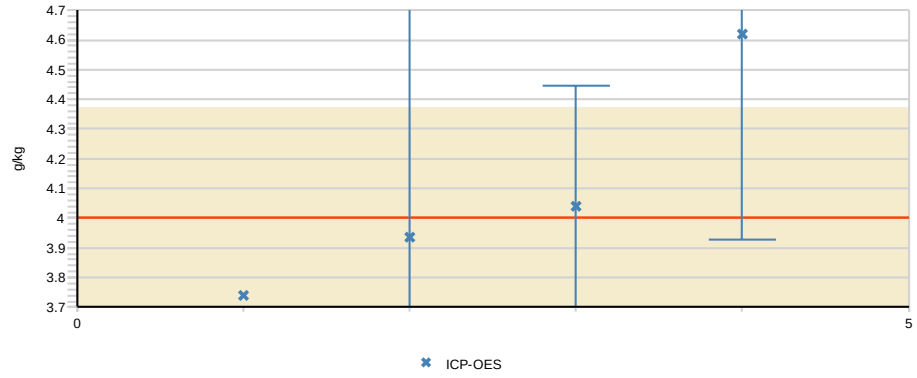

Measurand Se
Sample SN4
mg/kg
3.8
3.4
3
2.6
2.2
1.8
1.4
0
5
ICP-OES
ICP-MS


Measurand Se
Sample SO4
mg/kg
5.4
4.6
3.8
3
2.2
1.4
0.6
0
5
ICP-OES
ICP-MS

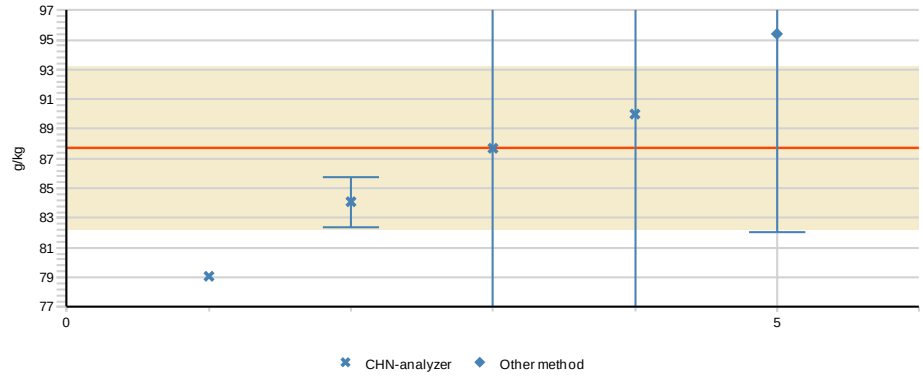
Measurand S_{tot} Sample SN4

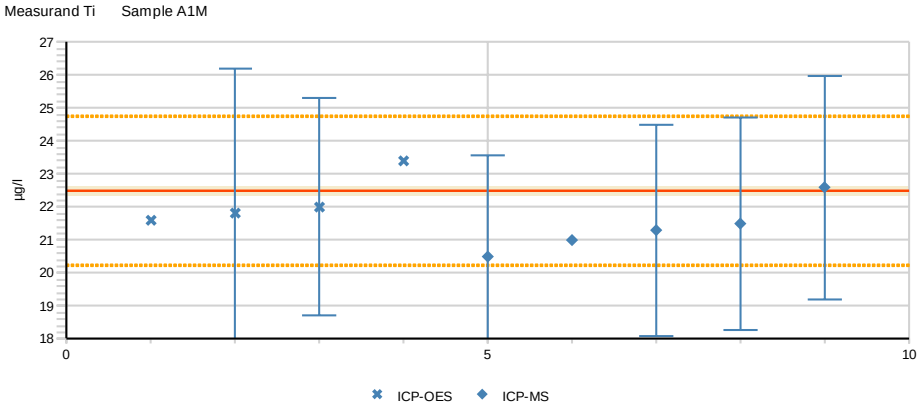


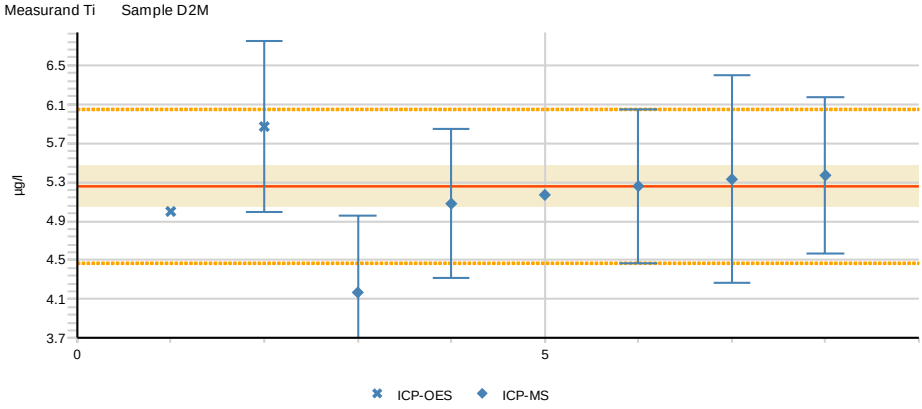
Measurand S_{tot} Sample SO4

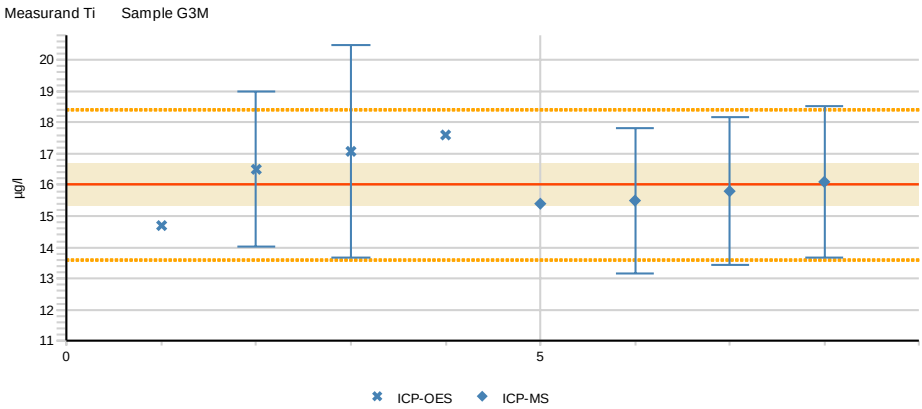


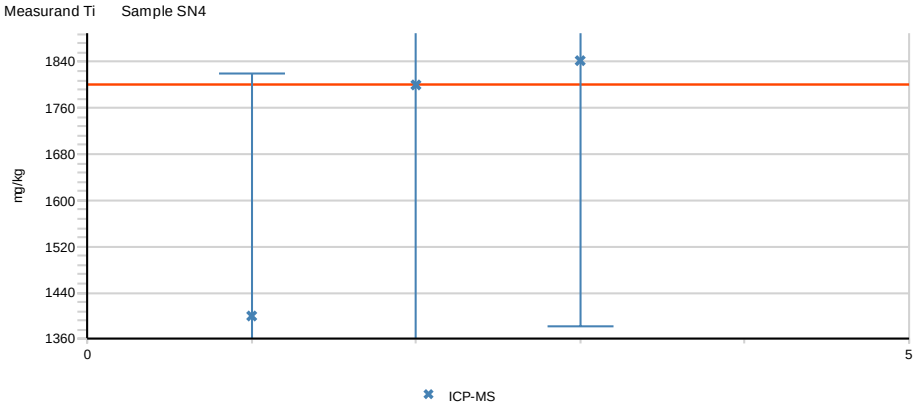
Measurand TC Sample S4M

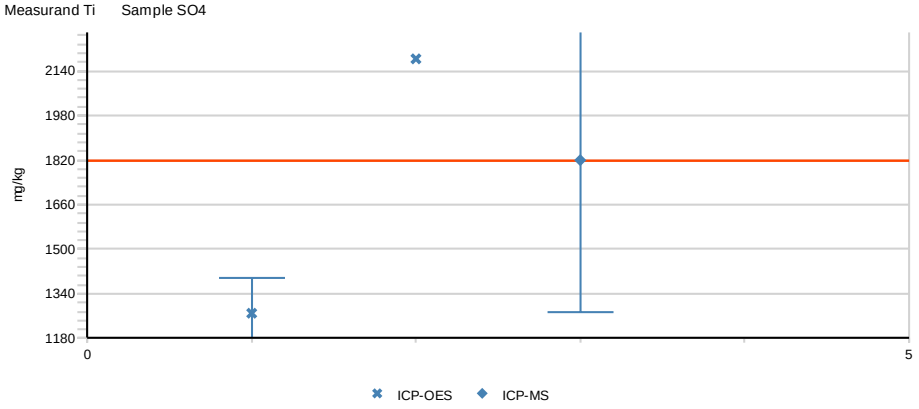


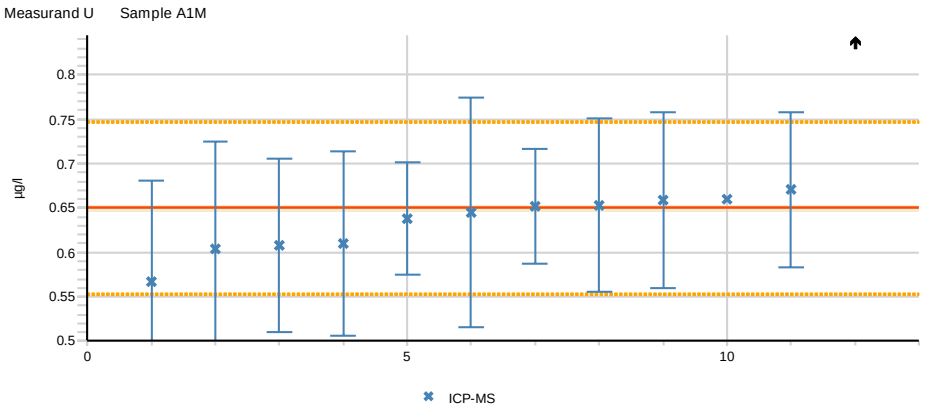

Measurand Ti Sample A1M
µg/l
27
26
25
24
23
22
21
20
19
18
0
5
10
ICP-OES
ICP-MS

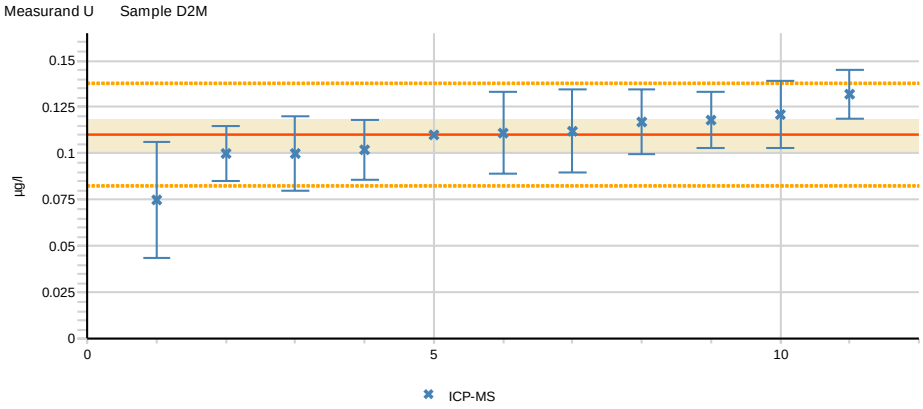

Measurand Ti Sample D2M
µg/l
6.5
6.1
5.7
5.3
4.9
4.5
4.1
3.7
0
5
ICP-OES
ICP-MS

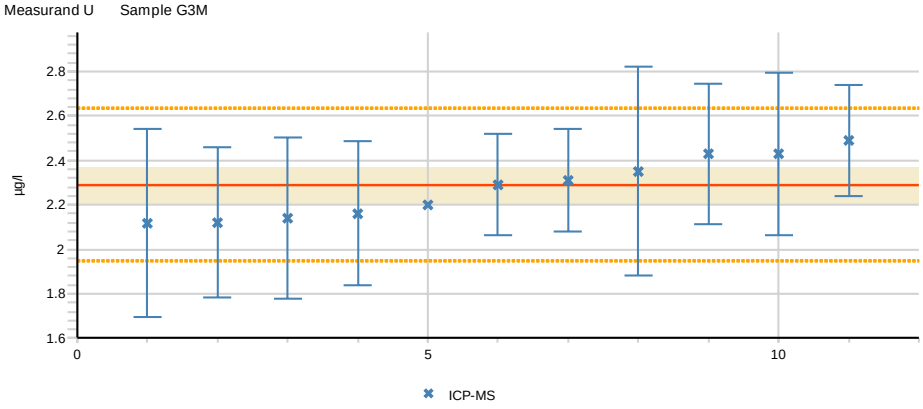

Measurand Ti Sample G3M
µg/l
20
19
18
17
16
15
14
13
12
11
0
5
ICP-OES
ICP-MS

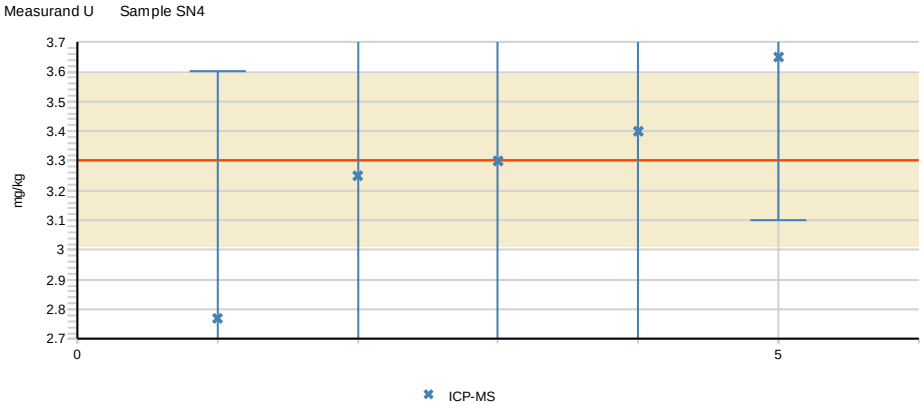

Measurand Ti Sample SN4
mg/kg
1840
1760
1680
1600
1520
1440
1360
0
5
ICP-MS


Measurand Ti Sample SO4
mg/kg
2140
1980
1820
1660
1500
1340
1180
0
5
ICP-OES
ICP-MS

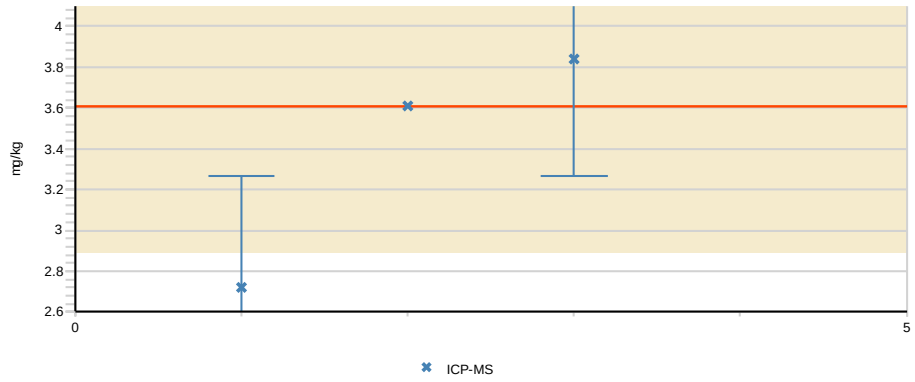

Measurand U Sample A1M
µg/l
0.8
0.75
0.7
0.65
0.6
0.55
0.5
0
5
10
ICP-MS


Measurand U
Sample D2M
µg/l
0.15
0.125
0.1
0.075
0.05
0.025
0
0
5
10
ICP-MS

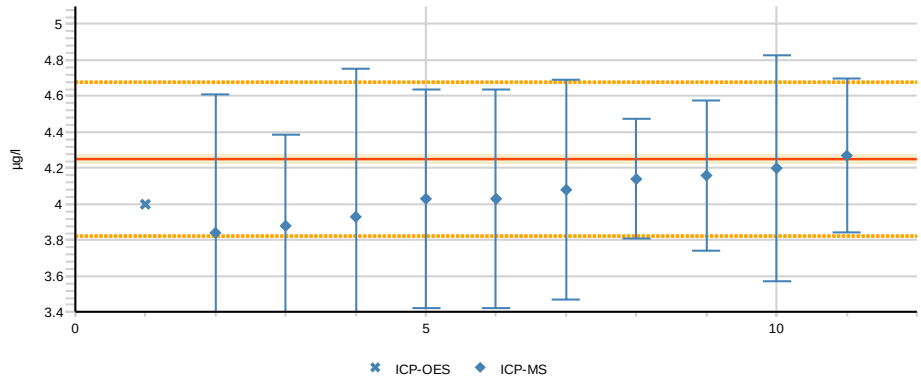

Measurand U
Sample G3M
µg/l
2.8
2.6
2.4
2.2
2
1.8
1.6
0
5
10
ICP-MS


Measurand U
Sample SN4
mg/kg
3.7
3.6
3.5
3.4
3.3
3.2
3.1
3
2.9
2.8
2.7
0
5
ICP-MS

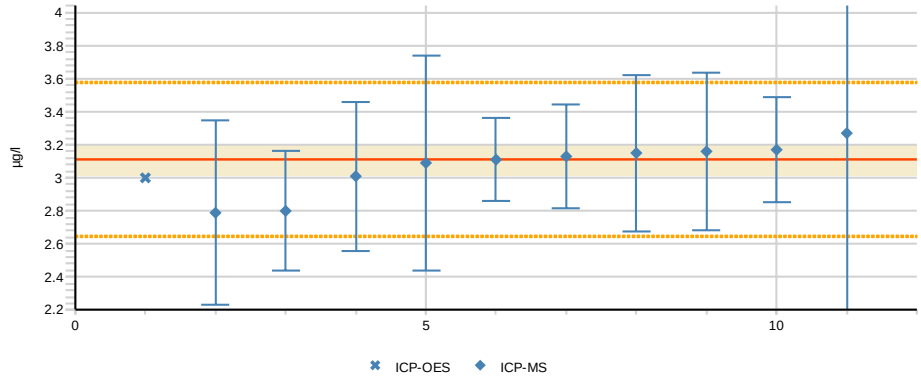
Measurand U Sample SO4



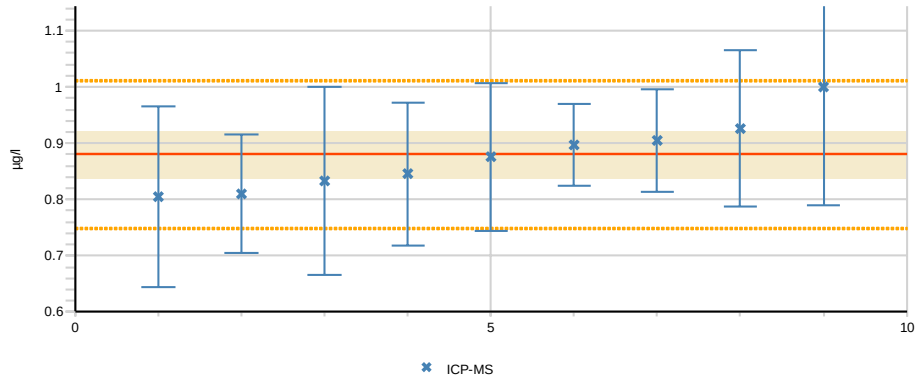
Measurand V Sample A1M



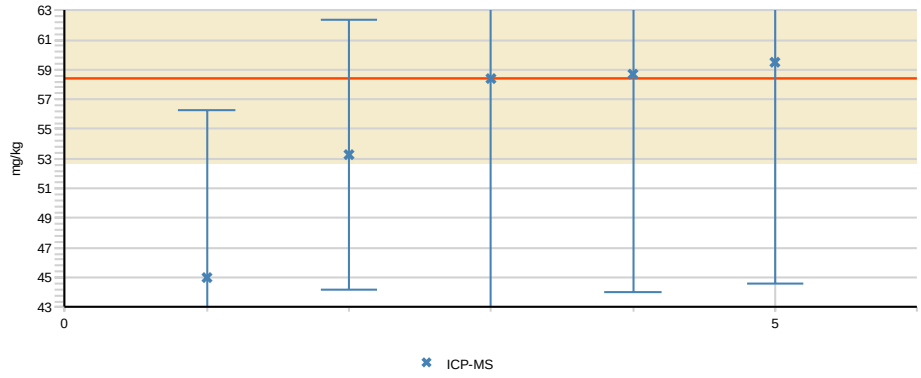
Measurand V Sample D2M



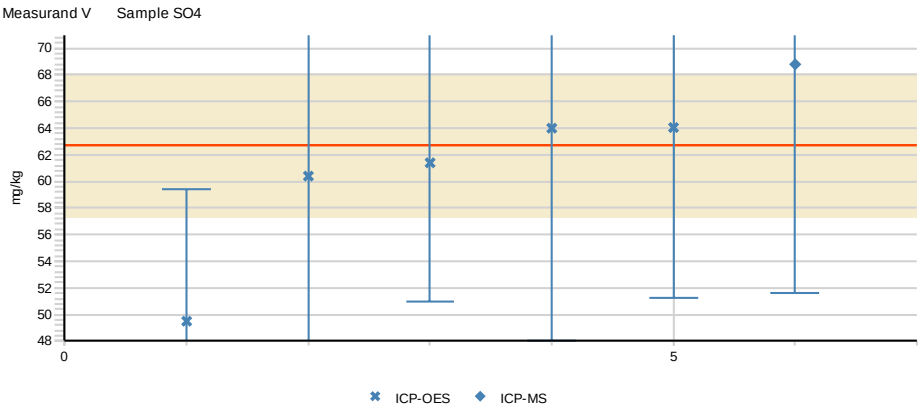
Measurand V Sample G3M



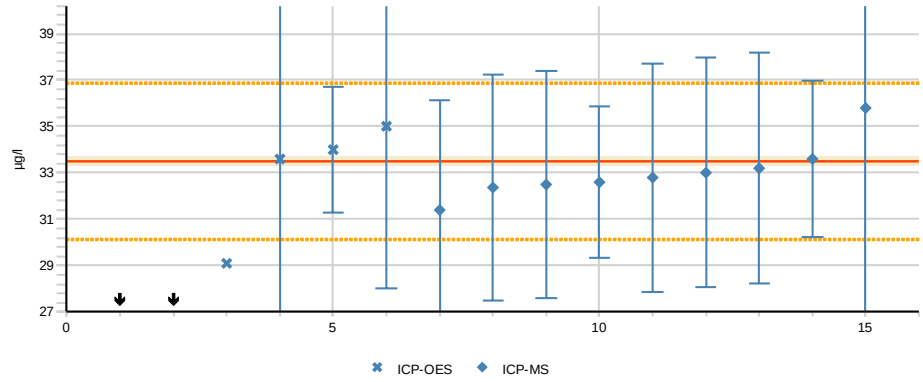
Measurand V Sample SN4



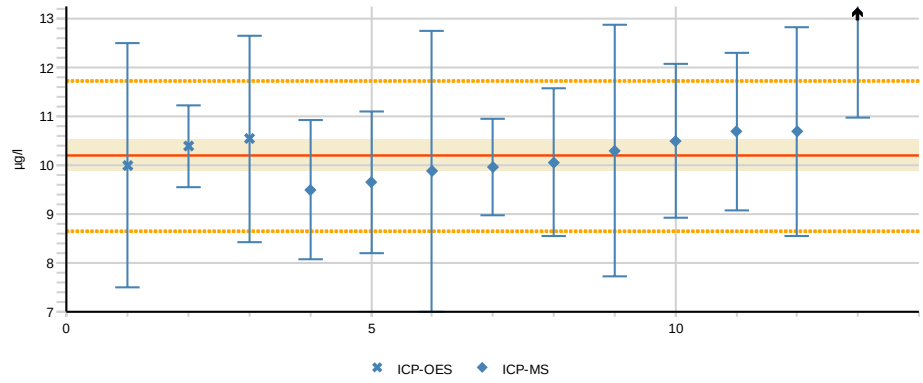
Measurand V Sample SO4



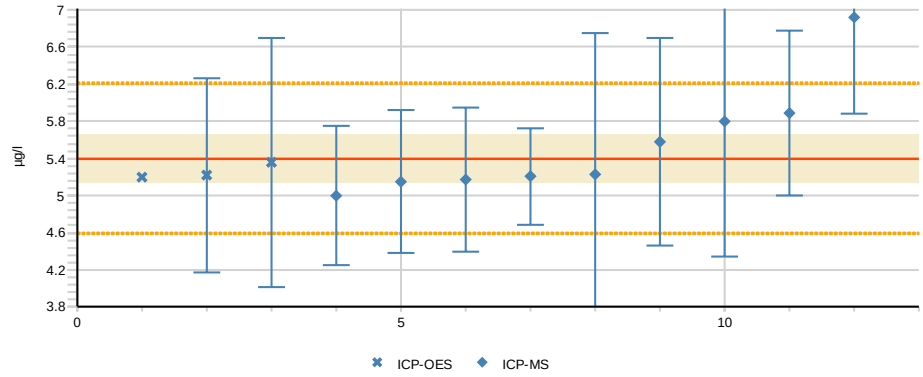
Measurand Zn Sample A1M

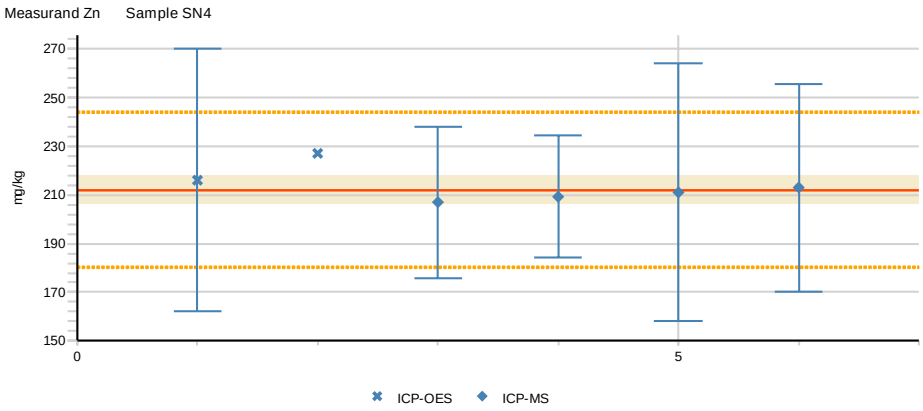


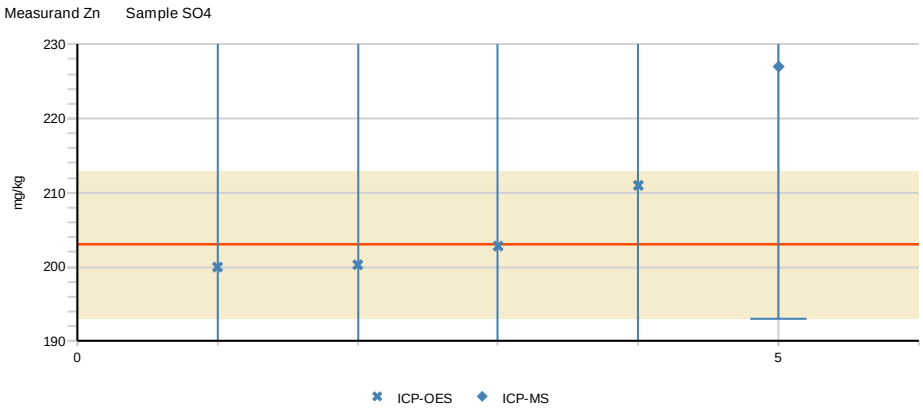
Measurand Zn Sample D2M



Measurand Zn Sample G3M



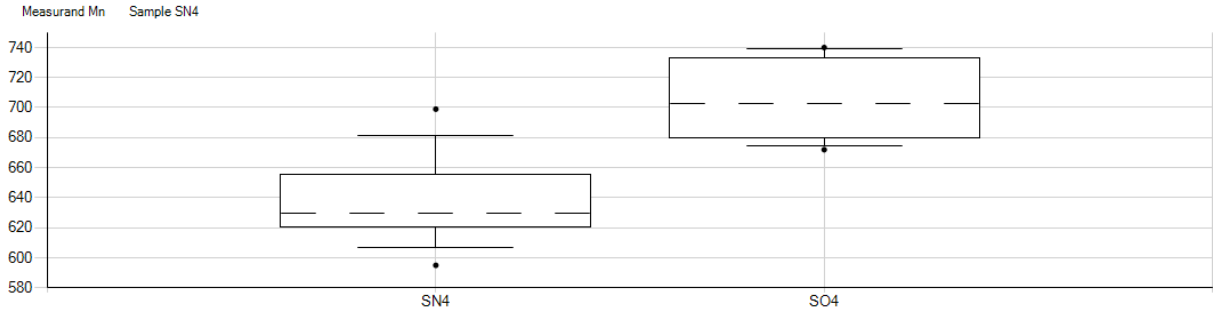

Measurand Zn
Sample SN4
mg/kg
270
250
230
210
190
170
150
0
5
ICP-OES
ICP-MS


Measurand Zn
Sample SO4
mg/kg
230
220
210
200
190
0
5
ICP-OES
ICP-MS

APPENDIX 12: Significant differences in the results reported using different methods

Boxplot figures: In the box the upper and lower limit included 50 % of the results. The dashed vertical line in the middle of the box is the median of the results. The vertical lines above and under the box describe the limits of 80 % of the results. The black dots describe the highest and smallest results within the center 90 % of the results.

Statistically significant differences between pretreatment methods, sediment sample

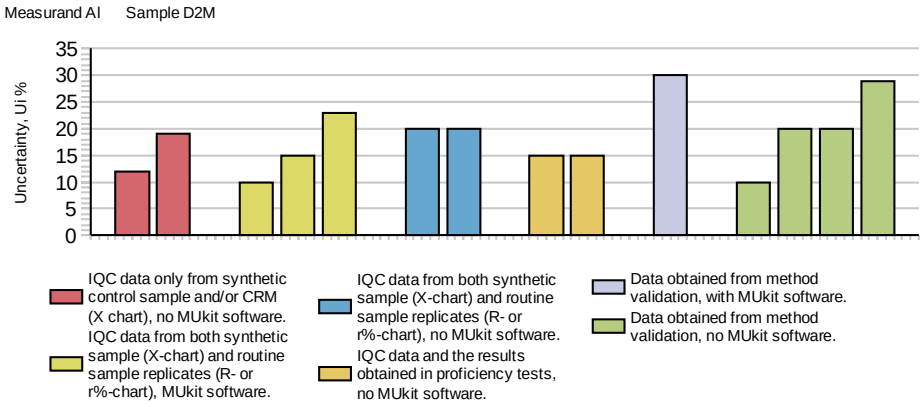


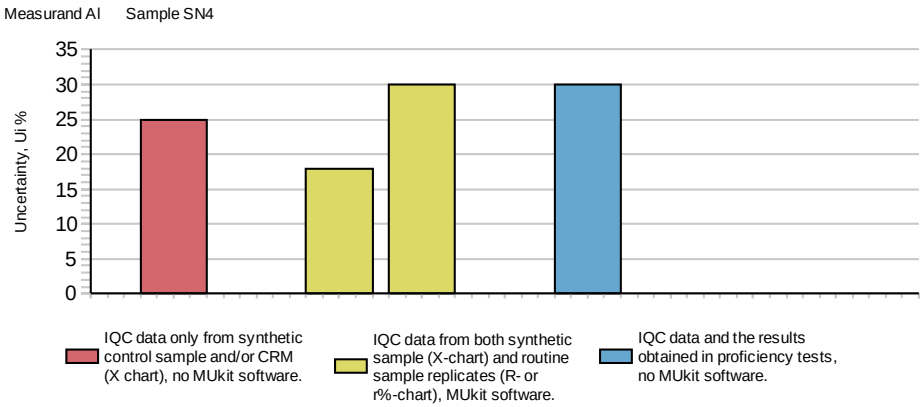
Method	s	Mean (mg/kg)	Median (mg/kg)	s (mg/kg)
SN4: digestion with HNO_3	6	639	630	37
SO4: digestion with HNO_3+HCl	6	705	702	31

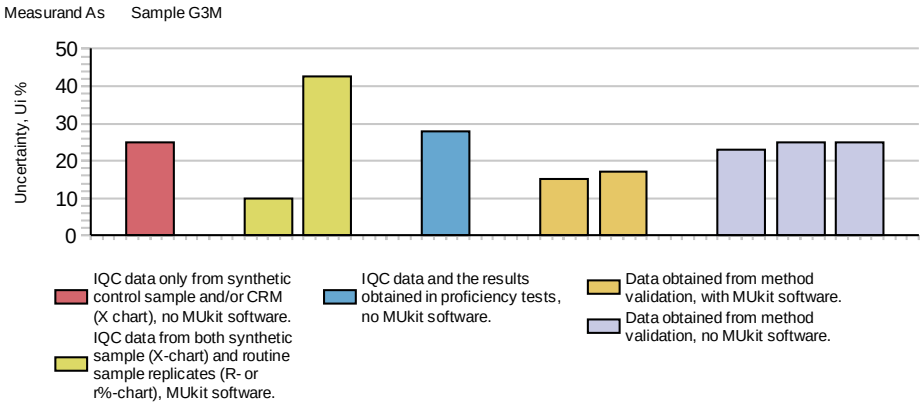
n=number of results; s=standard deviation

APPENDIX 13: Examples of measurement uncertainties reported by the participants

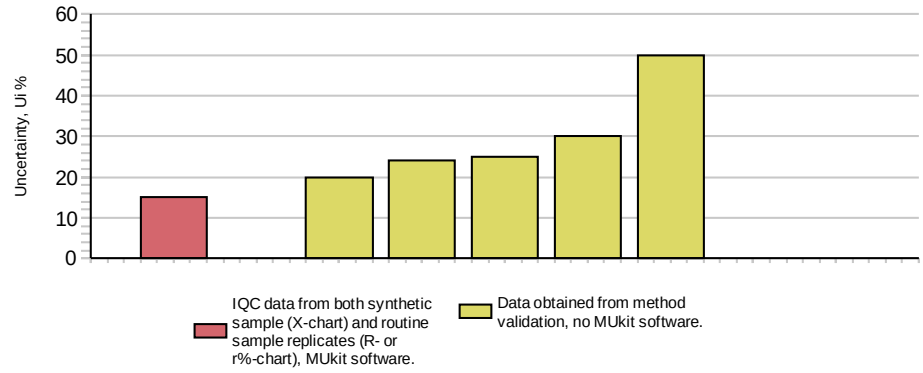
In figures, the presented expanded measurement uncertainties are grouped according to the method of estimation at 95 % confidence level (k=2). The expanded uncertainties were estimated mainly by using the internal quality control (IQC) data. The used procedures in figures below are distinguished e.g. between using or not using the MUkit software for uncertainty estimation [8, 9].



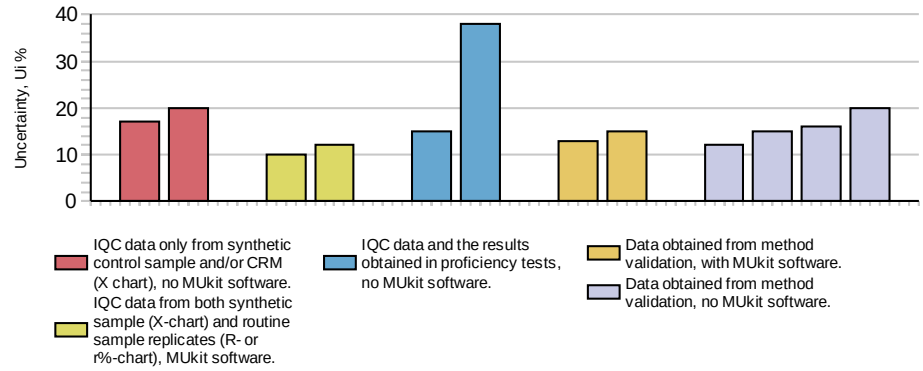




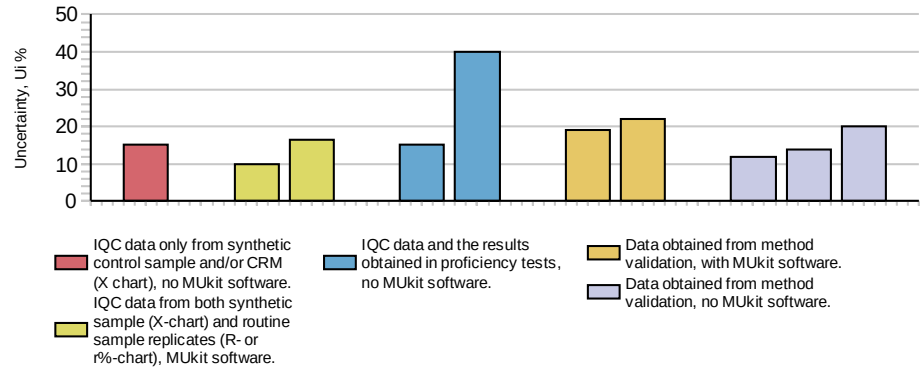
Measurand As Sample SO4



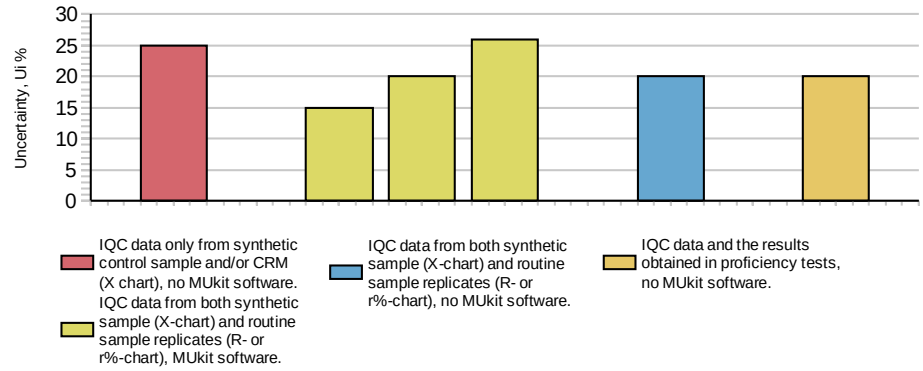
Measurand Cd Sample A1M



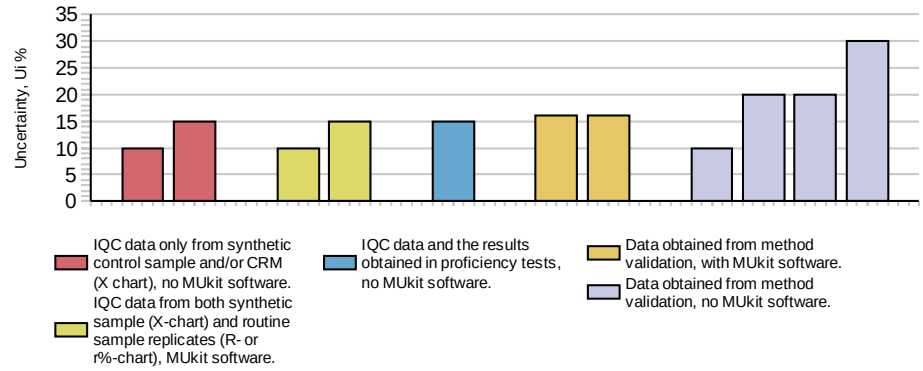
Measurand Co Sample D2M



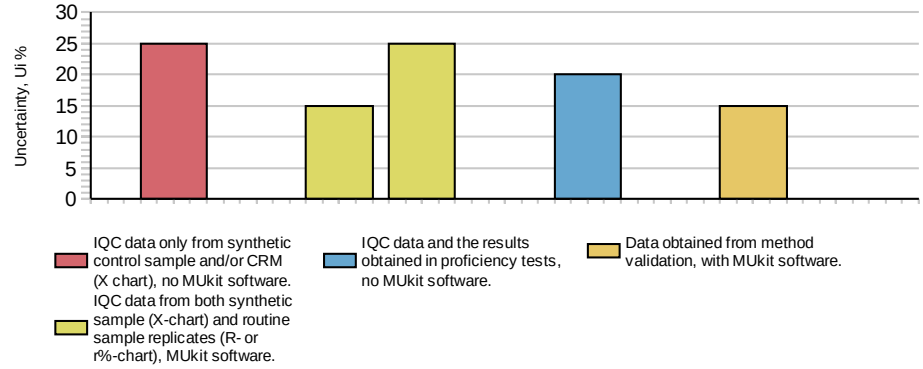
Measurand Cr Sample SN4



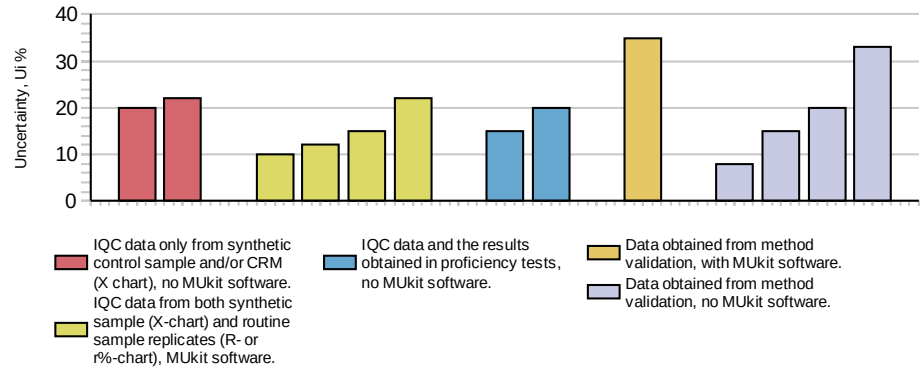
Measurand Cu Sample G3M



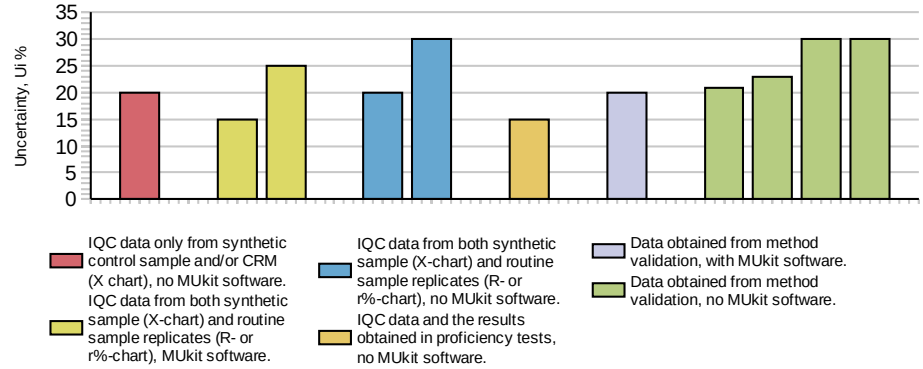
Measurand Cu Sample SN4



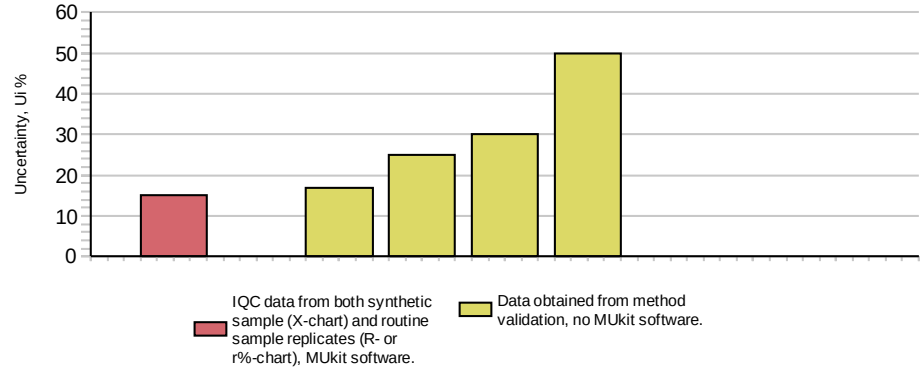
Measurand Fe Sample G3M

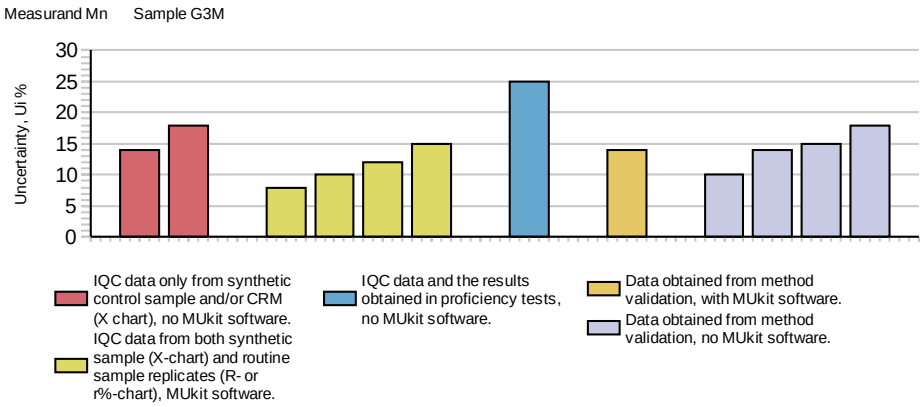


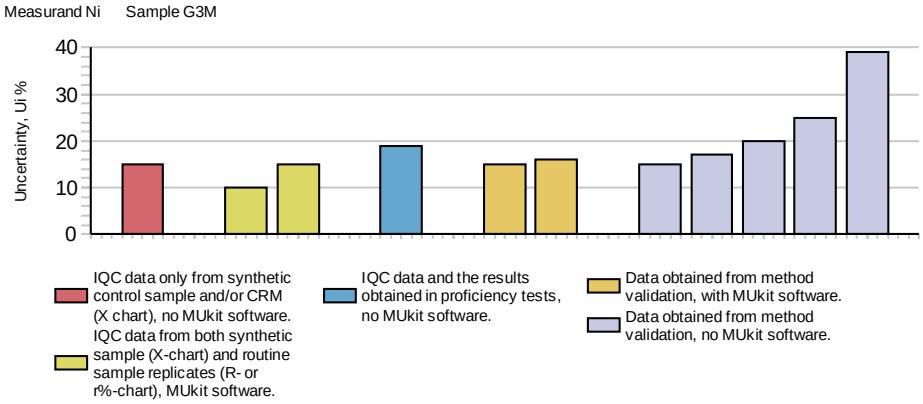
Measurand Hg Sample D2Hg

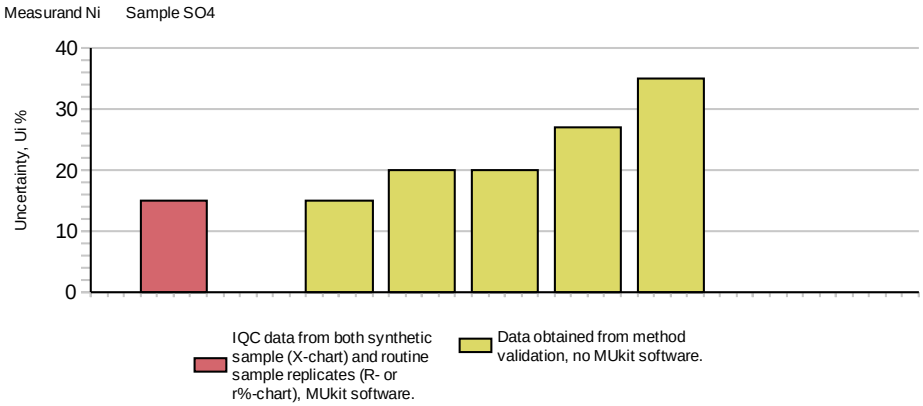


Measurand Hg Sample SO4

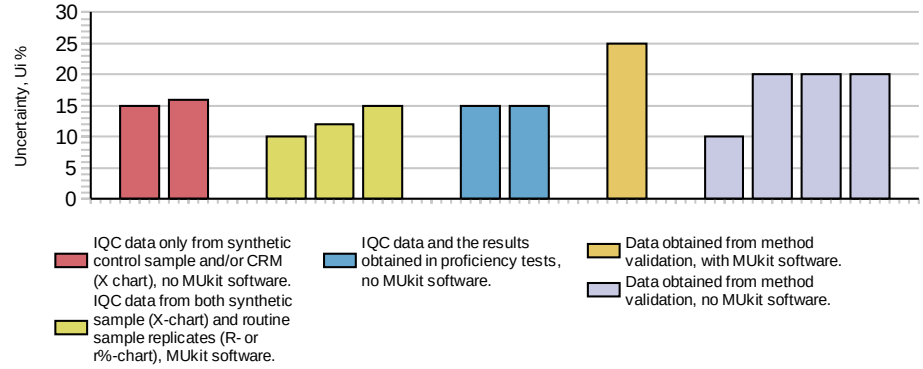



Measurand Mn Sample G3M
Uncertainty, Ui %
30
25
20
15
10
5
0
IQC data only from synthetic control sample and/or CRM (X chart), no MUkit software.
IQC data and the results obtained in proficiency tests, no MUkit software.
Data obtained from method validation, with MUkit software.
Data obtained from method validation, no MUkit software.
IQC data from both synthetic sample (X-chart) and routine sample replicates (R- or r%-chart), MUkit software.

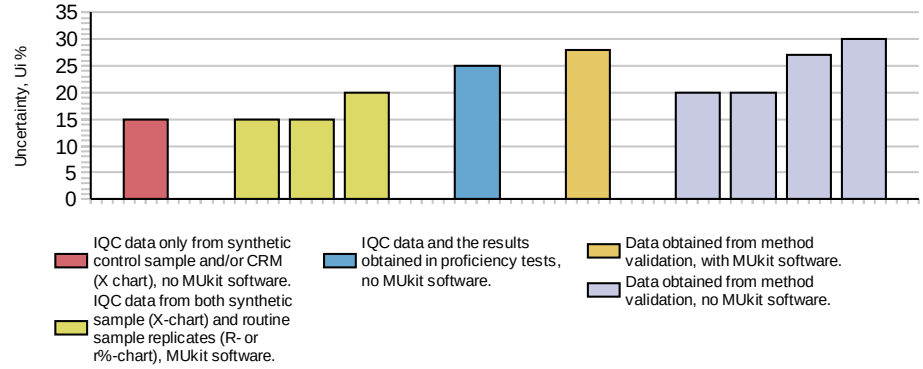

Measurand Ni Sample G3M
Uncertainty, Ui %
40
30
20
10
0
IQC data only from synthetic control sample and/or CRM (X chart), no MUkit software.
IQC data and the results obtained in proficiency tests, no MUkit software.
Data obtained from method validation, with MUkit software.
Data obtained from method validation, no MUkit software.
IQC data from both synthetic sample (X-chart) and routine sample replicates (R- or r%-chart), MUkit software.


Measurand Ni Sample SO4
Uncertainty, Ui %
40
30
20
10
0
IQC data from both synthetic sample (X-chart) and routine sample replicates (R- or r%-chart), MUkit software.
Data obtained from method validation, no MUkit software.

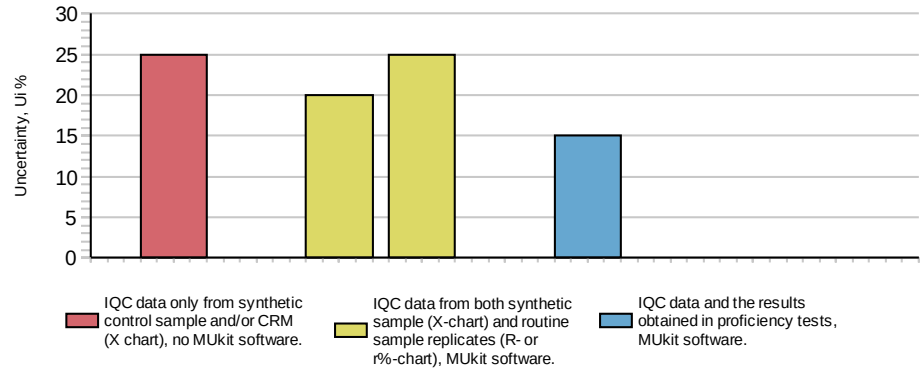
Measurand Pb Sample D2M

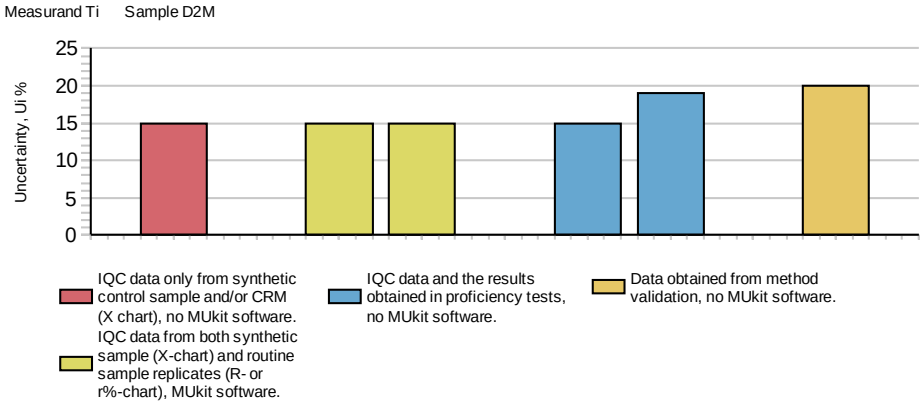


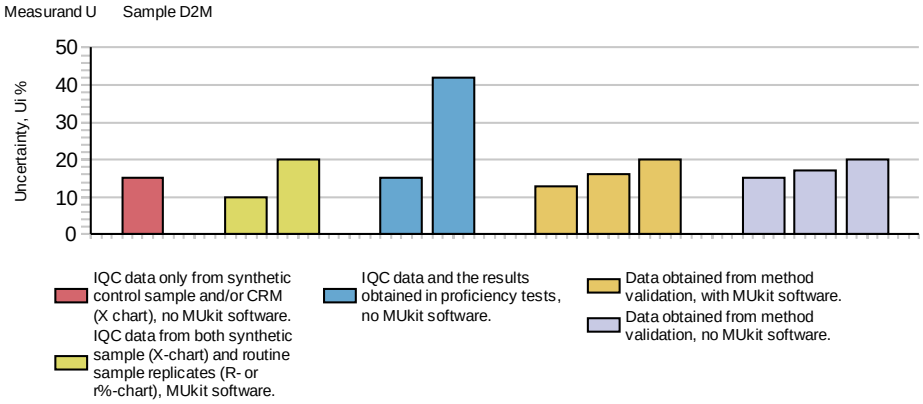
Measurand Se Sample G3M



Measurand S_{tot} Sample SN4




Measurand Ti Sample D2M
Uncertainty, Ui %
25
20
15
10
5
0
IQC data only from synthetic control sample and/or CRM (X chart), no MUkit software.
IQC data and the results obtained in proficiency tests, no MUkit software.
Data obtained from method validation, no MUkit software.
IQC data from both synthetic sample (X-chart) and routine sample replicates (R- or r%-chart), MUkit software.


Measurand U Sample D2M
Uncertainty, Ui %
50
40
30
20
10
0
IQC data only from synthetic control sample and/or CRM (X chart), no MUkit software.
IQC data and the results obtained in proficiency tests, no MUkit software.
Data obtained from method validation, with MUkit software.
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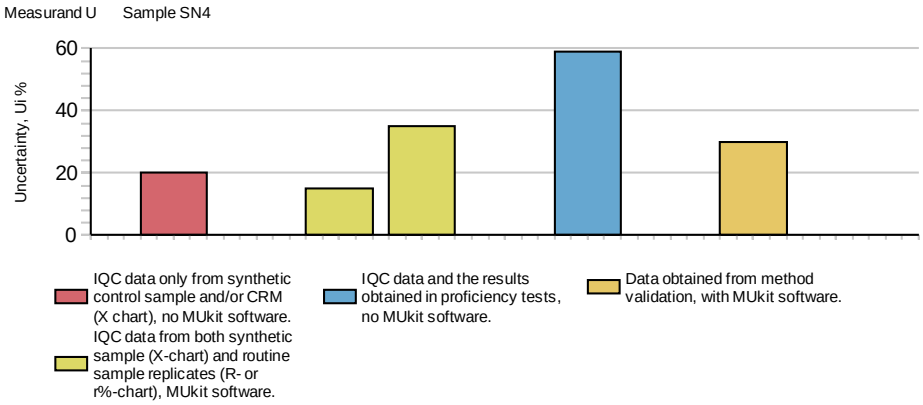
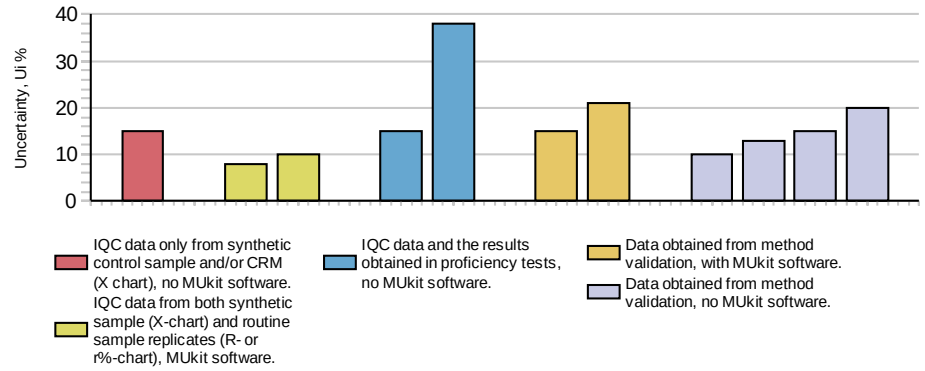
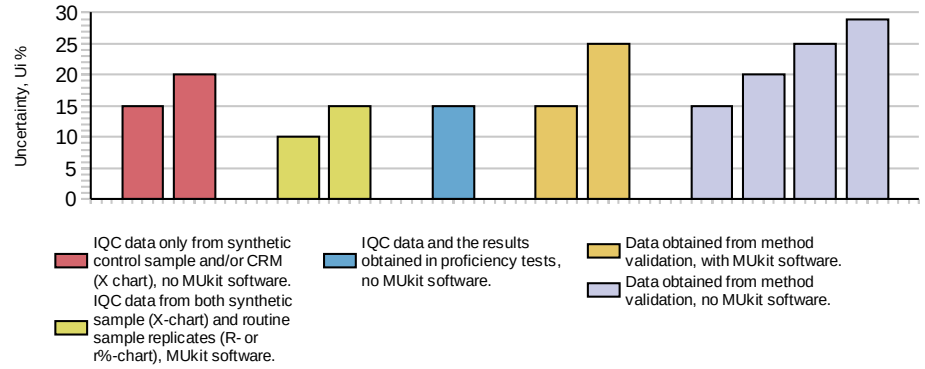
IQC data from both synthetic sample (X-chart) and routine sample replicates (R- or r%-chart), MUkit software.


Measurand U Sample SN4
Uncertainty, Ui %
60
40
20
0
IQC data only from synthetic control sample and/or CRM (X chart), no MUkit software.
IQC data and the results obtained in proficiency tests, no MUkit software.
Data obtained from method validation, with MUkit software.
IQC data from both synthetic sample (X-chart) and routine sample replicates (R- or r%-chart), MUkit software.

Measurand V Sample D2M



Measurand Zn Sample G3M



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